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WADC TECHNICAL REPORT 57-126

PART IV

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PHOSPHINOBORINE POLYMERS

Ross I. Wagner

*American Potash & Chemical Corporation
Research Department
Whittier, California*

Best Available Copy

AUGUST 1960

WRIGHT AIR DEVELOPMENT DIVISION

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PART IV

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Ross I. Wagner

*American Potash & Chemical Corporation
Research Department
Whittier, California*

AUGUST 1960

Materials Central
Contract No. AF 33(616)-5435
Project No. 1428

WRIGHT AIR DEVELOPMENT DIVISION
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared by American Potash & Chemical Corporation, Research Department, Whittier, California, and by Dr. Anton B. Burg and co-workers at the University of Southern California, Los Angeles 7, California. The report covers work done under U.S.A.F. Contract No. AF 33(616)-5435. The contract was initiated under Project 1428 "Secondary Power Components and Materials"; Task No. 73313, "Hydraulic Fluids," and was administered under the direction of the Materials Central, Dir. of Adv. Systems Technology, Wright Air Development Division, with Dr. Robert L. Adamczak, acting as Project Engineer.

This report covers work conducted from January 6, 1959 through January 5, 1960.

The report is divided into two parts as follows: "Phosphinoborine Polymers," by American Potash & Chemical Corporation (Contract No. AF 33(616)-5435); and "Chemistry of Inorganic Polymer Components," by Dr. Anton B. Burg and co-workers (Contract No. AF 33(616)-5435, Subcontract No. AF-5435-1).

The work at American Potash & Chemical Corporation Laboratories was carried out under the direction of Dr. W. S. Emerson, Manager, Research, and Dr. K. R. Eilar, Assistant Manager, Research, and Head, Organic Chemistry Section. This report was prepared by Dr. Ross I. Wagner who acted as project leader. The laboratory work was conducted primarily by Drs. Frederick F. Caserio, Jr., Marvin H. Goodrow and Darwin L. Mayfield and Messrs. LeVern D. Freeman, Gordon F. Dierks, Harley J. Rockoff, James L. Bradford, John J. Cavallo, James R. Peter, and Stanley E. Iversen.

ABSTRACT

A series of preparations of linear dimethyl-, methylethyl- and diethylphosphinoborine polymers have been made to optimize experimental conditions. N-Methylpiperazine when used as an end-group for linear dimethylphosphinoborine polymers provided a fair yield of product which, except for a large melting range, resembled polymers terminated with other end-groups. Triethylenediamine markedly reduced the rate of dimethylphosphine borine pyrolysis and failed to yield a linear polymeric product. Qualitative solubility data have been obtained for the linear methylethyl- and diethyl- derivatives. Attempts to prepare linear phosphinoborine polymers either by pyrolysis of trimethylphosphine trichloroborine or dimethylphosphinoborine trimer with triethylamine or by alkylation of methylphosphinodimethylborine polymer were unsuccessful. Linear methylethylphosphinoborine polymer was only partially chlorinated on treatment with methyl chloride--aluminum chloride in contrast to the dimethyl-derivative. A further attempt to open the dimethylphosphinoborine trimer ring by heating with triethylenediamine resulted instead in a polymer formed by opening the ring structure of the diamine.

Dimethylphosphinoborine trimer was prepared in good yield from dimethylphosphonium chloride and lithium borohydride and in low yield by dehydrohalogenation of dimethylphosphine chloroborine. Dehydrohalogenation of dimethylphosphine diethylchloroborine and dimethylphosphine trichloroborine failed to give cyclic trimeric products but the latter appeared to yield low molecular weight linear phosphinoborine polymers. The stoichiometry of the fluorination of dimethylphosphinoborine trimer has been established experimentally but no success has been achieved in attempts to cyanogenate the trimer. An X-ray diffraction study of the dimethylphosphinoborine--methylphosphinoborine pentamer indicated the crystals to be of complex structure. Dimethylphosphinodichloroborine trimer appears to be less thermally stable than the parent compound.

The synthesis of phosphine intermediates by known methods has produced one new secondary phosphine and one new organophosphine derivative. Nuclear magnetic resonance spectra of the phosphine, C_2H_5P , prove it to be cycloethylenephosphine rather than the isomeric vinylphosphine.


N-Dimethyl-B-trimethylborazene has been synthesized both by dehydrohalogenation of a mixture of the methyldibromoborine adducts of methylamine and ammonia and by pyrolysis of a mixture of the trimethylborine adducts of methylamine and ammonia. The isomeric N-trimethyl-B-dimethylborazene was prepared by reaction of N-trimethylborazene with a deficiency of methylmagnesium bromide. The attempt to prepare decamethylbiborazyl by pyrolytic dehydrogenation of the two isomeric pentamethylborazenes resulted in formation of by-product methane and a polymeric borazene derivative. The pseudoaromatic 8-bora-7,9-diazaro-peri-naphthene has been prepared and studied briefly.

Dimethyl- and diphenylthiosiloxane polymers have been prepared by reaction of the corresponding dichlorosilanes with hydrogen sulfide. In the presence of trimethylchlorosilane the preparation of diphenylthiosiloxane polymers resulted in a high yield of a single crystalline solid, presumably the trimer or dimer.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

A handwritten signature in cursive script that reads "A. M. Lovelace".

A. M. LOVELACE
Chief, Polymer Branch
Nonmetallic Materials Laboratory
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I. INTRODUCTION

The primary objective of this program is to conduct research in the field of polymeric materials which are basically inorganic in nature and are capable of development into elastomers, adhesives and/or fluids having extreme chemical and thermal stability. The program embraces primarily the field of phosphinoborines but includes work on borazenes and thiosiloxanes as well.

The phosphinoborines offer a promising field of study since as a class, these compounds are unusually resistant to thermal decomposition and to oxidative and hydrolytic attack.

The two basic approaches to the problem of preparing useful compounds are (1) altering the substituents on the inorganic skeletal atoms, and (2) changing the degree of polymerization. The changes in physical and chemical properties resulting from varying substituents or changing degree of polymerization are in the phosphinoborine field to be compared with the properties of trimeric dimethylphosphinoborine, $[(CH_3)_2PBH_2]_3$, as the reference standard.

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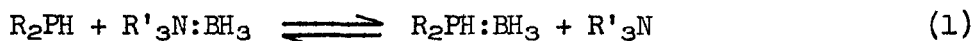
II. DISCUSSION

A. Phosphinoborines

1. Linear Phosphinoborine Polymers

a. Dimethylphosphinoborine Polymer

Several additional experiments summarized in Table I were performed to further delineate reaction variables which may influence the yield or degree of polymerization of linear dimethylphosphinoborine polymer. In some of the experiments the previously reported¹ procedure using a phosphine borine and an amine end-group was employed while in other experiments triethylamine borane was used as the boron source. The pyrolysis presumably proceeds according to the general equations (1) and (2):



(1) Pyrolysis of Dimethylphosphine Borine in the Presence of N-Methylpiperazine

Pyrolysis of dimethylphosphine borine in the presence of N-methylpiperazine led to formation of 129.7% yield of hydrogen and a 38.1% yield of polymer which appeared from its infrared spectrum to be identical with linear dimethylphosphinoborine polymer terminated by other end-groups. The product had a rather large melting range and may be a mixture of amino- and phosphinoborine polymers or a phosphinoborine polymer cross-linked through tetracoordination of the secondary amino function of N-methylpiperazine preceded by B-N bond formation with elimination of hydrogen.

(2) Pyrolysis of Dimethylphosphine Borine in the Presence of Triethylenediamine

In two experiments, the pyrolysis of dimethylphosphine borine in the presence of triethylenediamine did not lead to high molecular weight linear polymer but instead yielded mostly volatile products which were not investigated and a small amount of nonvolatile material which was identified as triethylenediamine bis(borine). The time required to complete the pyrolyses as judged by hydrogen evolution was considerably greater than pyrolyses done in the presence of triethylamine.

Triethylenediamine borine and bis(borine) have been prepared for reference purposes by direct reaction of triethylenediamine with one-half and one mole of diborane, respectively.

(3) Dimethylphosphinoborine Polymer from Dimethylphosphine and Triethylamine Borane

Linear dimethylphosphinoborine polymer, prepared from dimethylphosphine and triethylamine borane in a 1:1 mole ratio, was comparable to that

TABLE I
Results of Experiments on Preparation
of Linear Dimethylphosphinoborine Polymers

Expt.	(CH ₃) ₂ PHBH ₃ Used cc. (gas STP)	Et ₃ NBH ₃ Used cc. (gas STP)	End-group Used cc. (gas STP)	R ₃ N: (CH ₃) ₂ PHBH ₃ Mole Ratio	Reaction		Products	
					Time, Hrs.	Temp., °C.	H ₂ Yield, %	Polymer Yield, % m.p., °C.
37	179.1	0	CH ₃ N(C ₂ H ₄) ₂ NH	0.55	20	200	126.3	38.1 166-230
38	176.5	0	N(C ₂ H ₄) ₃ N	0.44	20	200	70.5	- -
39	169.8	0	N(C ₂ H ₄) ₃ N	0.39	40	200	89.2	- -
40	0	115.8	(CH ₃) ₂ PH	1.03	15	200	100.2	54.9 167-69
41	0	108.2	(CH ₃) ₂ PH /(C ₂ H ₅) ₂ NCH ₂ /2	1.21	15	200	97.4	62.2 161-63
42	0	115.9	(CH ₃) ₂ PH (C ₂ H ₅) ₃ N	1.17	15	200	100.1	60.5 166-68

prepared from dimethylphosphine borine and triethylamine. In two other preparations, addition of N,N,N',N'-tetraethylethylenediamine and triethylamine appeared to have only a small effect on the yield of polymer.

b. Methylethylphosphinoborine Polymer

A series of 17 pyrolysis experiments of a mixture of methylethylphosphine and triethylamine borane has been performed on a 3-6 mmole scale in order to determine optimum conditions for preparation of linear methylethylphosphinoborine polymer. The results of the pyrolyses, which presumably proceed according to Equations (1) and (2) (vide supra), are summarized in Table II.

Inclusion of N,N,N',N'-tetraethylethylenediamine in experiment 60 resulted in a 63.9% yield of methylethylphosphinoborine polymer having m.p. 119-20°C. The melting point is not significantly different from those obtained in preparations having no diamine present. A molecular weight determination will be necessary to see if the diamine acted as a "middle group" and thus increased the molecular weight of the linear polymer.

c. Diethylphosphinoborine Polymer

In two experiments, diethylphosphinoborine linear polymer has been prepared from diethylphosphine and triethylamine borane in 46.2 and 42.5% yields. The products had melting points of 257-58°C. and 257-59°C., respectively. The latter experiment contained added triethylamine.

d. Attempt to Form Linear Dimethylphosphinoborine Polymer from Cyclic Trimer by Pyrolysis in the Presence of Tertiary Amines

A previous attempt to prepare dimethylphosphinoborine linear polymer² by pyrolysis of the trimer and triethylamine at 200°C. failed. A second attempt to produce linear polymer by this method at 350°C. was equally unsuccessful.

In several experiments, dimethylphosphinoborine trimer and triethylenediamine were pyrolyzed at 200°C. and 350°C. to yield mostly starting materials and some nonvolatile high melting solid. This solid contained no B-H links and was proved to arise from decomposition of triethylenediamine by its formation during pyrolysis of the diamine alone. The nonvolatile product is possibly a linear polymer formed by scission and intermolecular recombination of one carbon-nitrogen bond per decomposed molecule of diamine. A cross-linked polymer is also possible if more than one carbon-nitrogen scission occurred per decomposed diamine molecule.

e. Attempt to Prepare Methylallylphosphinoborine Polymer

The previously reported attempt to prepare methylallylphosphinoborine polymer³ resulted in a presumably somewhat cross-linked low molecular weight polymer but the data were insufficient to determine whether the olefinic linkage had been destroyed by addition of a P-H or B-H bond to it or by vinyl polymerization. Accordingly a freshly prepared sample of methylallylphosphine borine was analyzed by infrared. The spectrum indicated that the borine group initially had attached

TABLE II

Results of the Pyrolysis of
Methylethylphosphine and Triethylamine Borane

Expt.	CH ₃ (C ₂ H ₅) ₃ P Used, mmoles	(C ₂ H ₅) ₃ NBH ₃ Used, mmoles	(C ₂ H ₅) ₃ N Added, mmoles	Reaction Time Hrs.	Reaction Temp., °C.	% Yield Product		Polymer m.p., (a) °C.
						H ₂	Polymer	
43	5.595	5.735	-	8	200	98.6	-	-
44	5.701	5.239	-	8	200	98.1	53.3	103-10
45	6.228	7.017	-	15	200	104.5	35.4	116-18
46	5.951	6.703	-	15	200	101.2	8.2	93-98
47	5.828	4.107	-	8	180	87.3	31.7	45-50(b)
48	5.291	3.684	-	15	180	-	71.5(b)	93-98(b)
49	5.732	6.439	-	8	190	90.7	73.3(b)	95-100(b)
50	5.374	5.522	-	9	190	98.1	50.8	93-95
51	6.306	3.169	-	9	190	93.8	106(c)	90-95
52	5.590	3.106	-	9	190	-	47.8	80-82
53	5.700	5.099	5.32	9	190	107.4	60.6	116-18
54	5.532	5.906	5.72	9	190	100.9	68.4	116-18
55	6.109	6.212	0.688(d)	9	190	90.6	37.4	102-104
56	6.348	6.526	-	15	190	-	69.4(b)	105-12(b)
57	5.279	5.522	(e)	15	190	101.2	60.0	118-19
58	5.863	5.867	17.86	15	190	107.2	44.5	118-19
59	5.391	5.522	0.71	15	190	100.5	70.2	119-22
60	6.038	6.212	0.059(f)	15	200	100.9	62.9	119-20

(a) Taken on micro hot stage.

(b) Sublimation performed at 120°C.; product contains volatile material.

(c) Apparently erroneous; see Expt. 52.

(d) Triethylenediamine.

(e) About 200 mg. of stainless steel filings added to reaction tube.

(f) N,N,N',N'-Tetraethylethylenediamine.

to phosphorus rather than added across the carbon unsaturation. Upon standing ten days the adduct was transformed from a fluid liquid into a slightly tacky solid with a concomitant decrease in unsaturation.

f. Attempt to Prepare Dimethylphosphinodichloroborine Polymer

(1) Dehydrohalogenation of Dimethylphosphine Trichloroborine

The dehydrohalogenation of dimethylphosphine trichloroborine in benzene solution with a stoichiometric quantity of triethylamine was approximately 90% complete, based upon analysis of the by-product ammonium salts. On fractional solution of the crude product a fraction which analyzed as the triethylamine adduct of linear dimethylphosphinodichloroborine trimer was isolated. Based on the assumed trimer-adduct structure the yield was 15%. A 42% yield of a material which was apparently linear dimethylphosphinodichloroborine was obtained by further fractional solution of the remaining crude product. No dimethylphosphinodichloroborine trimer was isolated in accord with previous results^{4,5}.

(2) Pyrolysis of Trimethylphosphine Trichloroborine

An attempt was made to prepare dimethylphosphinodichloroborine polymer by liberation of methyl chloride on pyrolysis of trimethylphosphine trichloroborine. No change of the adduct occurred at 350°C. during 20 hrs. Analysis of the products obtained at 500°C. indicated complete decomposition of the phosphine moiety with little effect on the borine moiety.

g. Dimethylphosphinodichloroborine Polymer

The chlorination of linear dimethylphosphinoborine polymer to give a 31.7% yield of linear dimethylphosphinodichloroborine polymer has been accomplished in conventional laboratory glassware. The infrared spectrum of the product showed a small B-H absorption indicating that the reaction did not quite go to completion. The melting point of the product was 215-25°C. under nitrogen and above 360°C. in air. Apparently the compound is oxidized in air during a melting point determination and the previously reported⁶ melting point of above 360°C., which was taken in air, must be disregarded. Unfortunately, none of the polymer previously prepared using high vacuum techniques remains for a redetermination of its melting point.

h. Reaction of Methylethylphosphinoborine Polymer with Methyl Chloride--Aluminum Chloride

Chlorination of methylethylphosphinoborine linear polymer with methyl chloride and aluminum chloride did not proceed beyond 53.7-57.7% completion giving products which in two cases were brittle solids, m.p. 70-75°C. and in one case a viscous liquid. The solid products decomposed with a loss in weight to a viscous liquid during several days storage at room temperature. The odor of phosphine was always present over the products. Possible explanations for the incomplete chlorination could be either that steric requirements might limit replacement of hydrogen to about 60% of the theoretical or that aluminum chloride causes decomposition of the polymer and itself loses activity.

i. Determination of the Density of Linear Dimethylphosphinoborine Polymer

The density of dimethylphosphinoborine polymer (D.P. 80) was determined by the flotation method to be 1.012 g./ml. at 24.2°C. in the presence of a wetting agent. A value of 0.982 g./ml., determined in the absence of a wetting agent was probably slightly in error due to trapped air on the surface of the polymer.

j. Molecular Weight of Dimethylphosphinoborine Polymer after Treatment with Boron Trifluoride

A molecular weight of the product from treatment of dimethylphosphinoborine polymer (D.P. 80) with boron trifluoride⁶ was determined in benzene at 91.8°C. by the isopiestic method with azobenzene as the standard. The value, 14,479, obtained after correction for a small amount of insoluble material in the polymer was the highest yet observed and corresponds to D.P. 195.

k. Solubilities of Methylene- and Diethylphosphinoborine Polymers

The solubilities of methylene- and diethylphosphinoborine polymers were tested qualitatively in most of the common organic solvents and in some very unusual solvents for the latter polymer. The diethyl derivative was found to be insoluble in all common organic solvents and in all the unusual solvents except refluxing naphthalene from which it could not be recovered, presumably because of depolymerization. The methylene-derivative was found to be soluble in benzene and cyclohexane at room temperature; in acetone, triethylamine, Skelly F and *n*-pentane in sealed tubes just above their boiling points; and in refluxing *n*-hexane, which proved to be the most practical solvent for reprecipitation of the polymer for purification purposes. The data are summarized in Table III.

l. Attempt to Prepare Dimethylphosphinodimethylborine Polymer

The fully alkylated linear phosphinoborine polymer, dimethylphosphinodimethylborine, was not obtained by treatment of linear methylphosphinodimethylborine polymer with either methyllithium or sodium amide, followed, in both cases, by methyl bromide. Both metallic reagents apparently cleaved the P-B bond as did sodium metal⁷ rather than metalating the polymer. The predominant product obtained from the reaction with methyllithium was trimethylphosphine trimethylborine, indicating the reaction sequence shown in Equations (3) and (4).



A similar degradation of methylphosphinodimethylborine explaining the formation of aminodimethylborine trimer and dimethylphosphine is outlined in Equations (5) and (6).

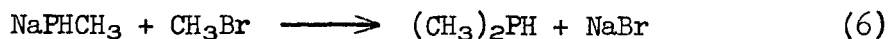
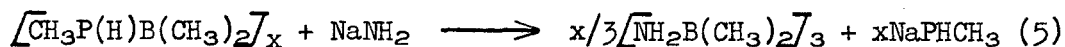


TABLE III
Solubility of Linear
Methylethylphosphinoborine Polymer

Solvent	Solubility ^(a)		
	Cold	Hot	Cooled
Methanol	-	-	-
Benzene	+		
Acetone	-	+(b)	-
Triethylamine	-	+	+
Cyclohexane	+(c)		
Skelly F	-		
	-	+(d)	
Petroleum ether (20-40°C.)	-	-	
<u>n</u> -Pentane	-	-	
		+(d)	
<u>n</u> -Hexane (99%)	-	+	-(e)
<u>n</u> -Hexane (95%)	-	+	-(e)

(a) + Signifies completely soluble, clear solution;

- signifies solid present.

(b) Cloudy solution.

(c) Slow solution.

(d) Under pressure in a closed tube at ca. 100°C.

(e) Flocculent precipitate formed with clear supernatant liquid on cooling slowly at room temperature. Slightly gummy precipitate formed if cooled rapidly.

2. Cyclic Phosphinoborine Polymers

a. Dimethylphosphinoborine Trimer and Tetramer from Dimethylphosphonium Chloride and Lithium Borohydride

The interaction of lithium borohydride and dimethylphosphonium chloride in ether followed by solvent removal and pyrolysis gave a 72.3% yield of dimethylphosphinoborine trimer and tetramer mixture.

b. Dimethylphosphinoborine Trimer by Dehydrohalogenation of Dimethylphosphine Chloroborine

Dimethylphosphine chloroborine, prepared by treating dimethylphosphine borine with hydrogen chloride, was dehydrohalogenated in ether solution with triethylamine. Based on the by-product ammonium salts the resulting dehydrohalogenation was 65% complete. An 11.7% yield of dimethylphosphinoborine trimer was obtained by fractional sublimation of the crude product.

c. Attempt to Prepare Dimethylphosphinodiethylborine trimer by Dehydrohalogenation of Dimethylphosphine Diethylchloroborine

An ethereal solution of dimethylphosphine diethylchloroborine was treated with triethylamine. Analysis of the by-product ammonium salts indicated that the resulting dehydrohalogenation was only 50-55% complete. Approximately 75% of the crude product was not recovered from an attempted recrystallization from methanol, evidently due to methanolysis of the material. The recovered portion contained no material which could be identified as dimethylphosphinodiethylborine.

d. Dimethylphosphinoborine--1,3-Trimethylene-P,P'-bis(methylphosphinoborine) Copolymers

In order to obtain corroboration for the two-ring bridged structure proposed⁸ for one of the products of the copolymerization of dimethyl- and 1,3-trimethylene-P,P'-bis(methylphosphinoborine)s another similar compound was sought in the benzene soluble residues of the copyrolysis. By an involved series of high vacuum fractional sublimations, 0.8 and 3.2 mg. of purified colorless crystalline materials were isolated but the amounts of material obtained unfortunately were insufficient for meaningful analyses.

e. Reaction of Dimethylphosphinoborine Trimer with Cyanogen Bromide

In a further attempt to substitute hydrogen in dimethylphosphinoborine trimer by the cyano group, two experiments using cyanogen bromide were carried out under much more mild conditions than used previously⁹. In one experiment run at 100°C. in cyclohexane, cyanogen bromide and trimer reacted to produce impure tribromo-substituted trimer. No cyano groups could be detected in the product by infrared spectroscopy. The second experiment was carried out at room temperature and no reaction occurred since the starting trimer was quantitatively recovered.

f. Attempt to React Dimethylphosphinoborine Trimer with Cyanogen

In five separate vacuum line experiments, attempts were made to substitute hydrogen on boron in dimethylphosphinoborine trimer by the cyano group through interaction of trimer with cyanogen, prepared by pyrolysis of silver cyanide according to the procedure of Cook and Robinson.¹⁰ The variables examined were temperature, reaction time and presence of zinc cyanide, benzoyl peroxide or copper powder. In no case was any cyano-substituted trimer isolated; however, in the experiments carried out at high temperature or in the presence of zinc cyanide or benzoyl peroxide, small yields of the expected hydrogen cyanide by-product were detected by infrared analysis.

g. Dimethylphosphinodifluoroborine Trimer

Dimethylphosphinodifluoroborine trimer was prepared as previously reported¹¹ from dimethylphosphinoborine trimer and anhydrous hydrogen fluoride in 81% yield. After repeated recrystallization and sublimation, a sample was finally obtained which analyzed satisfactorily for carbon and hydrogen. In a larger scale experiment, the fluorinated trimer was prepared in 98% yield. The determination of the stoichiometry was completed by carrying out the reaction in a stainless steel bomb and measuring the hydrogen produced; 6.19 moles (103% of theoretical) of hydrogen was produced per mole of trimer.

h. X-ray Diffraction Study of Dimethylphosphinoborine--Methylphosphinoborine Copolymer

A preliminary X-ray study done by the Stanford Research Institute, Menlo Park, California, of the copolymer, $[(CH_3)_2PBH_2]_4CH_3PBH$, has shown the crystals to be strongly birefringent plates with the (001) plane as principal face. The unit cell dimensions, obtained from rotation and Weissenberg photographs of three crystals are:

$$\begin{aligned} a &= 8.70 \pm 0.02 & b &= 11.16 \pm 0.02 & c &= 12.89 \pm 0.02 \text{ \AA} \\ \alpha &= 100.0 \pm 0.5^\circ & \beta &= 106.3 \pm 0.5^\circ & \gamma &= 76.7 \pm 0.5^\circ \end{aligned}$$

An alternate choice of axial directions leads to the dimensions:

$$\begin{aligned} a &= 8.70 & b &= 15.53 & c &= 12.89 \text{ \AA} \\ \alpha &= 45.0^\circ & \beta &= 106.3^\circ & \gamma &= 66.6^\circ \end{aligned}$$

From the density 1.025 g./cm.³ (obtained by flotation) and the cell dimensions a molecular weight of 349 was calculated based on two molecules per unit cell. Observation of a strong positive piezoelectric effect indicated the unit cell has no center of symmetry and the space group is Pl.

B. Evaluation of Phosphinoborines

1. Thermal Stability of Dimethylphosphinodichloroborine Trimer

The thermal stability of dimethylphosphinodichloroborine trimer was cursorily studied at 357°C. by determination of the change in melting point of the

trimer. After 1 hr., the melting point had dropped at least 15°C. and the sample showed visible discoloration. In 2 hrs., the melting point had dropped more than 85°C. In 2-1/2 hrs., the sample had turned orange and exploded when placed in a melting point bath at 302°C.

C. Organophosphines

1. Methylallylphosphine

An improved isolation procedure resulted in an increase in yield of methylallylphosphine from the previously reported¹² 13% to 22%. A purer sample was used to redetermine some physical constants.

2. 3,3-Dimethylcyclotrimethylenephosphine

A preliminary experiment to prepare 3,3-dimethylcyclotrimethylenephosphine from sodium phosphinide and 1,3-dibromo-2,2-dimethylpropane yielded a volatile liquid which polymerized at room temperature. A second preparation, carried out under conditions of lower temperature and shorter reaction time, minimized the polymerization and made feasible the isolation and tentative characterization of 3,3-dimethylcyclotrimethylenephosphine.

3. Diethylphosphine from Tetraethylbiphosphine Disulfide

Tetraethylbiphosphinedisulfide was prepared in 46.0% yield following the procedure of Issleib and Tzschach,¹³ reported to give a 65.5% yield. By reduction of this compound with lithium aluminum hydride, diethylphosphine was prepared in 27.7% yield (70.0% reported¹³). An attempt made to increase the yield of tetraethylbiphosphine disulfide was unsuccessful. Inadvertent oxidation of the product during evaporation of the wash liquor while attempting to recover the dissolved product precluded a definitive result. The yield of tetraethylbiphosphine disulfide was only 28.1%.

Two further attempts to evaluate the preparation of diethylphosphine from the intermediate disulfide were made by reduction without prior isolation. The first method consisted of the reduction of the hydrolyzed tetraethylbiphosphine disulfide-containing reaction mixture; and the second, reduction of the reaction mixture without preliminary hydrolysis. The results of the first method were inconclusive due to oxidation of the product. The second method gave only a 30% yield of diethylphosphine.

4. Structure Determination of Cycloethylene-phosphine by Nuclear Magnetic Resonance

In order to decide between the vinyl or cycloethylene structure for the phosphine, C_2H_5P , obtained⁵ by the reaction of 1,2-dichloroethane with sodium phosphide in liquid ammonia, the nuclear magnetic resonance (nmr) spectra of the phosphine were determined through the courtesy of Drs. J. D. Roberts and M. C. Caserio at the California Institute of Technology. The proton resonance spectra, determined at both 40 and 60 megacycles, were extremely complex due to the apparent nonequivalence of the protons on carbon and their splitting by the phosphorus atom. However, the proton on phosphorus was clearly identified by its doublet character which arises from spin-spin coupling with the phosphorus

atom. Each line of this doublet was split into five lines by the four protons on carbon as predicted by simple theory. Further, the proton spectrum showed no resonance at low magnetic field strengths where vinyl-type protons normally appear. The P^{31} nmr spectrum was determined at 10 megacycles and found to consist of a doublet each line of which was split into 5-6 lines. Simple theory predicts a doublet having each line split into five lines for the cycloethylene structure and a triplet having each line split into two lines for the vinyl structure. The fact that 5-6 lines were observed instead of the predicted five is attributed to poor signal/noise ratio of the nmr instrument when cycled for P^{31} , the small spin-spin coupling between P^{31} and the protons on carbon, and the saturation observed because of the long relaxation time of P^{31} . The nmr spectra conclusively prove the structure as that of cycloethylenephosphine.

5. Dimethylphenylphosphine

Dimethylphenylphosphine was prepared for use as an intermediate from methylmagnesium bromide and phenyldichlorophosphine.

6. Attempt to Prepare p-Dimethylphosphino-phenyldichlorophosphine or Its Derivatives

Both the reaction of dimethylphenylphosphine and the aluminum chloride catalyzed reaction of its hydrochloride with phosphorus trichloride resulted in an evolution of hydrogen chloride but in neither case could any of the difunctional phosphine be isolated. Methylation of the crude reaction product with methylmagnesium bromide or reduction with lithium aluminum hydride resulted in formation of tars from which no identifiable materials could be obtained.

7. Attempt to Prepare Dimethylaminodiethynylphosphine

An attempt to prepare a secondary alkynylphosphine by way of the intermediate aminophosphine failed when the intermediate could not be prepared. Sodium acetylide failed to react with dimethylaminodichlorophosphine, while ethynylmagnesium bromide reacted to produce only intractable tars.

8. Bis(dimethylamino)chlorophosphine

Bis(dimethylamino)chlorophosphine was prepared in 60.7% yield for use as an intermediate in the preparation of methyl(chloromethyl)chlorophosphine.

9. Bis(dimethylamino)methylphosphine

Bis(dimethylamino)methylphosphine was obtained in 34.4% yield by the action of methylmagnesium bromide on bis(dimethylamino)chlorophosphine in ether solution at -70°C .

10. Methyldichlorophosphine

Bis(dimethylamino)methylphosphine was converted to methyldichlorophosphine in 44% yield by the action of anhydrous hydrogen chloride at 0°C .

11. Attempt to Prepare Methyl-
(chloromethyl)chlorophosphine

An attempt to prepare methyl(chloromethyl)chlorophosphine by treating methyldichlorophosphine with an ethereal solution of diazomethane at -65°C . produced a liquid fraction which proved to be starting material with a trace of what may be the product as determined by infrared analysis. A solid product, insoluble in ether, soluble in water, was also produced and is presumed to be a polyphosphonium salt.

D. Borines

1. Methyldibromoborine

Methyldibromoborine was prepared in 20% yield by maintaining a 2:1 mole ratio of boron tribromide to trimethylborine at 153°C . for 40 hrs. Consumption of trimethylborine was essentially complete. Dimethylbromoborine was also obtained in 38% yield, and 53% of the initial boron tribromide was recovered.

E. Borazenes

Efforts to prepare polymeric material containing borazene nuclei have been concentrated largely on the preparation of borazene derivatives containing either one or two reactive functional groups. Also a few pseudoaromatic boron-nitrogen compounds have been prepared and studied briefly.

1. N-Dimethyl-B-trimethylborazene

Pyrolysis of a 2:1 mixture of methylamine trimethylborine and ammonia trimethylborine at 380°C . provided N-methyl-B-trimethylborazene and N-dimethyl-B-trimethylborazene in 28.5% and 36.2% yields, respectively. The relatively large yield of the tetramethyl compound is not surprising since ammonia trimethylborine is reportedly converted to the borazene at 330°C .¹⁴ while a reaction temperature of $400-450^{\circ}\text{C}$. is reported for a similar conversion of methylamine trimethylborine.¹⁵ Formation of by-product methane was 95% of theory.

In an alternative synthesis a 2:1 mole ratio of the adducts methylamine methyldibromoborine and ammonia methyldibromoborine was dehydrohalogenated with triethylamine. A 10% yield of N-methyl-B-trimethylborazene and a 16% yield of N-dimethyl-B-trimethylborazene were obtained together with a considerable quantity of polymeric material.

2. Methylamine Trimethylborine
and Ammonia Trimethylborine

The combined product from two preparations of trimethylborine was absorbed in separate excess quantities of methylamine and ammonia to form the respective trimethylborine adducts, which will be copyrolyzed to form an additional quantity of a mixture of borazene derivatives including N-methyl-B-trimethyl- and N-dimethyl-B-trimethylborazenes.

3. N-Trimethyl-B-dimethylborazene

N-Trimethyl-B-dimethylborazene was prepared in only 8.3% yield by treating an ethereal solution of N-trimethylborazene with two equivalents of

ethereal methylmagnesium bromide. Detection of 27% of the initial boron as an ether insoluble fraction indicates that considerable hydrolysis occurred when the Grignard complex was destroyed. No product was isolated from a similar synthesis employing methylmagnesium iodide reported to produce N-trimethyl-B-dimethylborazene in 53% yield.¹⁶

4. Methylaminoborine Trimer

A total of 702 g. methylaminoborine trimer was prepared in 76.5% yield for use as an intermediate for N-trimethyl-B-dimethylborazene by the absorption of diborane in methylamine, followed by partial dehydrogenation of the methylamine borine adduct. This yield undoubtedly could be greatly improved by moderating the exothermic reaction.

5. Attempt to Prepare Decamethylbiborazyl

Pyrolysis in the liquid phase of an equimolar mixture of N-trimethyl-B-dimethylborazene and N-dimethyl-B-trimethylborazene at temperatures up to 390°C. resulted in the evolution of both hydrogen and methane and in the formation of low molecular weight polymeric borazene derivatives. Methane evolution, which became pronounced at about 380°C., probably results in further polymerization by cross-linking during the formation of polymeric borazene compounds.

6. Pyrolysis of N-Trimethyl-B-dimethylborazene

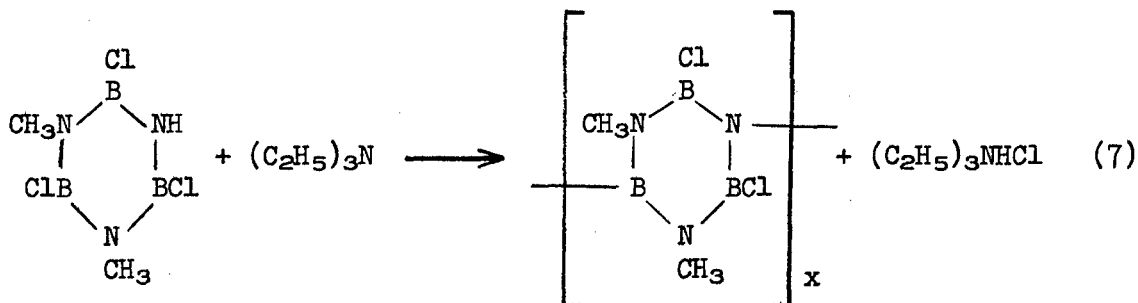
N-Trimethyl-B-dimethylborazene was heated in the vapor phase at temperatures up to 395°C. to determine if it is the source of methane in the attempted preparation of decamethylbiborazyl. The compound appeared to be stable in the vapor phase. Similar liquid phase pyrolyses of this compound and the isomeric N-dimethyl-B-trimethylborazene will be undertaken when sufficient quantities of these materials are available.

7. Pentamethyl-B-chloroborazene

Pentamethyl-B-chloroborazene assaying over 99% pure was prepared in 63% yield by methylation of N-trimethyl-B-trichloroborazene with two equivalents of ethereal methylolithium. The method of isolation apparently is crucial in this system. Removal of the reaction solvent by distillation rather than low temperature evaporation appeared to result in the destruction of the chloroborazene. The use of petroleum ether in lieu of benzene for extraction of the borazene values from the by-product lithium salts resulted in the isolation of a product which was purer than that previously attained.¹⁷

8. Attempt to Prepare N-Dimethyl-B-trichloroborazene

Dehydrohalogenation of a 2:1 mole ratio of methylamine trichloroborine to ammonia trichloroborine with triethylamine yielded a presumably polymeric material rather than N-dimethyl-B-trichloroborazene. Polymer formation may have arisen by the elimination of hydrogen chloride from the monomeric product as illustrated by Equation (7).



9. 8-Bora-7,9-diazaro-*peri*-naphthene and
8-Methoxy-8-bora-7,9-diazaro-*peri*-naphthene

In a reaction patterned after that reported by Dewar et al.,¹⁸ the new compound, 8-bora-7,9-diazaro-*peri*-naphthene, was prepared in 42.1% yield by interaction of boron trichloride with 1,8-diaminonaphthalene followed by treatment of the reaction mixture with lithium aluminum hydride. The product was characterized by its infrared spectrum, correct elemental analysis and methanolysis to the also new 8-methoxy-8-bora-7,9-diazaro-*peri*-naphthene which had the expected infrared spectrum and correct elemental analysis.

10. Pyrolysis of 8-Bora-7,9-diazaro-*peri*-
naphthene with Dimethylphosphine

A mixture of 8-bora-7,9-diazaro-*peri*-naphthene and dimethylphosphine was pyrolyzed in an attempt to determine whether the rigid nature of the boron-containing ring might cause formation of a linear phosphinoborine polymer. No adduct formed and after the pyrolysis, almost all of the dimethylphosphine was recovered unchanged. Approximately one mole of hydrogen per mole of starting material was liberated however, and from the solid product a 50.6% yield of a presumably polymeric substance was isolated which did not melt below 410°C. This product showed no B-H bands in its infrared spectrum but still possessed a N-H linkage and is possibly a polymer composed of a three-dimensional boron-nitrogen network or a borazene formed by trimerization of three monomer units.

F. Thiosiloxanes

1. Reaction of Diorganodichloro-
silanes with Hydrogen Sulfide

a. Dimethyldichlorosilane

Four different runs involving reaction of dimethyldichlorosilane with hydrogen sulfide in the presence of pyridine resulted in essentially similar yields of pyridine hydrochloride and light yellow liquid product whether the silane was added to excess H₂S or H₂S was introduced into excess silane as shown in Table IV. The molecular weight of the unpurified liquid was 187 ± 5 (calcd. for $[(\text{CH}_3)_2\text{SiS}]_2$, 180.45). This liquid on heating appeared to decompose with evolution of a gas yielding a solid which could be distilled at 175-200°C. The melting point of the purified solid, 109-12°C., is near that reported by Etienne¹⁹ (113°C.) for the cyclic dimethylthiosiloxane dimer. The molecular weight of the

TABLE IV

Preparation of Thiosiloxanes

Expt. No.	Reactants				Products				
	R_2SiCl_2		$\text{C}_5\text{H}_5\text{N}$		$\text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$		Liquid Intermediate	Solid	
	R	Wt., g.	Moles	Wt., g.	Moles	Wt., g.	Wt., g.	m.p., °C.	M.W.
1	CH_3	32.25(a)	0.25	39.5	0.50	-	12.1	109-12	-
2	CH_3	32.25(a)	0.25	39.5	0.50	ca. 40	15.0	-	-
3	CH_3	32.25(a)	0.25	39.5	0.50	41	15.1	111.5-13	218(b)
4	CH_3	32.25	0.25	39.5	0.50	42	15.2	-	-
5	C_6H_5	63.25(a)	0.25	39.5	0.50	ca. 40	-	135-80	840(b)
6	C_6H_5	63.25	0.25	39.5	0.50	ca. 53	-	110-80	-
7(f)	C_6H_5	63.25	0.25	45.8	0.58	56.5	9.8	192-94	594(b) 832(b,c) 448(d) 644(c,d)
8(g)	C_6H_5	65.53	0.26	57.4	0.73	60.75	14.92	193-94.5	-
9(h)	CH_3	32.25	0.25	47.5	0.60	39.2	15.12	111-13	-

(a) R_2SiCl_2 added to H_2S -saturated solution of pyridine in toluene.

(b) Cryoscopic in benzene by D.T.A.

(c) After heating to 350°C.

(d) Isopiestic in benzene (maximum values).

(e) Solid with some oil.

(f) 8.7 g. (0.08 mole) $(\text{CH}_3)_3\text{SiCl}$ present.(g) 12.4 g. (0.11 mole) $(\text{CH}_3)_3\text{SiCl}$ present.(h) 11.0 g. (0.10 mole) $(\text{CH}_3)_3\text{SiCl}$ added in two portions.

solid product, 218 ± 10 , does not correspond to the dimeric formula nor to that of a cyclic trimer (M.W. 270.68) of melting point $106-7^\circ\text{C}$. claimed to have been formed in a comparable manner by Moody.²⁰

b. Diphenyldichlorosilane

Reaction of diphenyldichlorosilane with hydrogen sulfide in the presence of pyridine, summarized in Table IV, resulted in a better yield of solid product if H_2S were introduced into an excess of the silane rather than the reverse (90.0% compared to 73.2% based on starting silane). The solid material appeared to be similar in each case, melting over a wide range which was not narrowed appreciably by recrystallization. Heating the solid to 240°C . resulted in no obvious gas evolution but the melting point range was narrowed from about $110-80^\circ\text{C}$. to $135-55^\circ\text{C}$. The molecular weight of the heated solid is above 850 which is far above the value of 428 (calcd. 428.74) reported by Moody²⁰ for the cyclic diphenylthiosiloxane dimer, m.p. $145-47^\circ\text{C}$.

2. Attempts to Detect Sulfhydryl Groups in Thiosiloxane Products

The sulfhydryl group has infrared absorption bands of such low intensity that its spectrophotometric detection is not practical if the sulfhydryl group is not a major portion of the molecule. To determine if the reaction products formed on treatment of either diphenyldichlorosilane or dimethyldichlorosilane with hydrogen sulfide in the presence of pyridine contain sulfhydryl groups, these products, free of H_2S , were treated in the presence of pyridine with either dimethyldichlorosilane or with trimethylchlorosilane. In benzene solution the formation of a precipitate of pyridine hydrochloride would offer evidence of reaction between a sulfhydryl group and the organochlorosilane. Only traces of precipitate resulted in each of several experiments which were conducted suggesting that the major portion of the thiosiloxane products are cyclic.

3. Reaction of Diorganodichlorosilanes with Hydrogen Sulfide in the Presence of Trimethylchlorosilane

a. Diphenyldichlorosilane

Whereas reaction of diphenyldichlorosilane with hydrogen sulfide in the presence of pyridine produces solid material in appreciable yield which melts over a wide range (ca. $110-80^\circ\text{C}$.) even after repeated recrystallization, substitution of a part of the diphenyldichlorosilane by small quantities of trimethylchlorosilane produces good yields [70-75% based on $(\text{C}_6\text{H}_5)_2\text{SiS}$] of a homogeneous white crystalline material (m.p. $192-94^\circ\text{C}$.) and a residual viscous tan oil, some of which could be distilled at approximately $240-60^\circ\text{C}/5\text{ mm}$. (M.W. 720). The infrared spectrum of neither the solid nor the distilled oil showed evidence of the presence of aliphatic C-H groups or $\text{CH}_3\text{-Si}$ bonding.

The crystalline solid showed a M.W. of 594 by the cryoscopic D.T.A. method but an isopiestic determination indicated a lower value (448) which appeared only to be a maximum. The material evolved hydrogen sulfide slowly on exposure to moist air but the melting point was lowered only two degrees on ten days standing on an open watch glass. A mixed melting point of this compound with an authentic sample of hexaphenylcyclotrisiloxane²¹ (m.p. $188-89^\circ\text{C}$.) showed

conclusively that the crystalline product was not the siloxane trimer formed by a secondary hydrolysis reaction (mixed m.p. 145-65°C.). The elemental analysis of the solid corresponds closely to that of the $(C_6H_5)_2SiS$ unit. It would appear that it is a cyclic trimer or dimer.

The solid was changed on heating in an atmosphere of nitrogen at 245-60°C. for 3 hrs. followed by an unsuccessful attempt to distill at a pot temperature of 350°C./4 mm. The residue set to a clear glass with a weight loss of less than 2%. The M.W. by the cryoscopic D.T.A. technique was 832 but an isopiestic determination gave 644 as a maximum value.

b. Dimethyldichlorosilane

The reaction of dimethyldichlorosilane with hydrogen sulfide in the presence of trimethylchlorosilane appeared to take the same course as the experiments performed in the absence of the monohalide since the products and the amounts produced were similar.

III. EXPERIMENTAL

A. Phosphinoborines

1. Linear Phosphinoborine Polymers

a. Dimethylphosphinoborine Polymer

(1) Pyrolysis of Dimethylphosphine Borine in the Presence of N-Methylpiperazine

Condensed successively into a 40 ml. bomb tube containing 0.4369 g. (4.362 mmoles) of N-methylpiperazine were 179.1 cc. (7.991 mmoles) of dimethylphosphine and 91.9 cc. (4.10 mmoles) of diborane. The tube was sealed and heated at $200 \pm 5^\circ\text{C}$. for 20 hrs. The tube was opened and found to contain 232.3 cc. (10.36 mmoles, 126.3%) of hydrogen. The volatile material, which was not further investigated, was sublimed at $180 \pm 5^\circ\text{C}$. and weighed 0.6260 g. The nonvolatile material was removed from the tube with the aid of hot benzene in which it was difficultly soluble. The benzene was evaporated to leave 0.2254 g. (38.1%) of slightly yellow granular material, m.p. ca. 166°C . (becomes translucent) to 230°C . (becomes clear). An infrared spectrum of this material is essentially the same as that of linear dimethylphosphinoborine polymer.

(2) Pyrolysis of Dimethylphosphine Borine in the Presence of Triethylenediamine

(a) Triethylenediamine Borine

A solution of 0.7050 g. (6.2845 mmoles) of triethylenediamine in 5 ml. of benzene was treated on the vacuum line with 70.2 cc. (3.13 mmoles) of diborane for about 2.5 days at room temperature. No diborane was recovered and the benzene solution contained a small amount of white precipitate. The benzene was heated and all but a small amount of the insoluble material dissolved. The solution was filtered hot and the filtrate allowed to crystallize. The product was filtered to give 0.4666 g. (58.9%) of white crystals, m.p. $164-65^\circ\text{C}$. (corr.). Anal. calcd. for $\text{C}_6\text{H}_{15}\text{BN}_2$: C, 57.18; H, 12.00. Found: C, 57.30; H, 11.42. Work-up of the mother liquors gave 0.2437 g. (30.8%) more of impure product.

(b) Triethylenediamine Bis(borine)

A solution of 1.1115 g. (9.9394 mmoles) of triethylenediamine in 5 ml. of benzene was treated on the vacuum line with 317.6 cc. (14.17 mmoles) of diborane at room temperature for about 3.5 days. A total of 56.1 cc. (2.50 mmoles) of diborane was recovered corresponding to uptake of 95.6% of the theoretical based on the weight of starting diamine. The product was insoluble in benzene. Evaporation of the benzene left 1.3200 g. (94.8%) of a white powder, m.p. $>390^\circ\text{C.d.}$ Anal. calcd. for $\text{C}_6\text{H}_{18}\text{B}_2\text{N}_2$: C, 51.52; H, 12.97. Found: C, 51.53; H, 12.82.

(c) Attempt to Prepare Linear
Dimethylphosphinoborine Polymer

Condensed successively into a 40 ml. bomb tube containing 0.39 g. (3.5 mmoles) of triethylenediamine were 176.5 cc. (7.879 mmoles) dimethylphosphine and 88.5 cc. (3.95 mmoles) of diborane. The tube was sealed under vacuum and heated at $200 \pm 15^\circ\text{C}$. for 20 hrs. The tube was opened and found to contain 124.4 cc. (5.55 mmoles, 70.5%) of hydrogen. The volatile material was sublimed at $180 \pm 5^\circ\text{C}$. for about 10 mins. and amounted to 0.7299 g. which was not further investigated. The residue weighed 0.0896 g. (18.4%), m.p. ca. 345°C.d. (shrinks at 320°C.) and was identified as principally triethylenediamine bis(borine) by its infrared spectrum.

In a second pyrolysis on the same scale, the bomb tube was heated at 200°C . for 40 hrs. and 89.2% of the theoretical hydrogen was obtained. All but 16.7 mg. of the tube contents were volatilized at 180°C . This residue could not be positively identified but appeared to be a mixture in which the presence of B-H bonds was detected by its infrared spectrum.

(3) Dimethylphosphinoborine Polymer from
Dimethylphosphine and Triethylamine Borane

The results of the three pyrolyses are summarized in Table I and since each experiment was done in the same manner, only experiment 41 is described in detail.

By means of a micro-buret with a long capillary tip, 0.70 ml. (4.83 mmoles) of triethylamine borane was introduced into a 40 ml. heavy-wall Pyrex tube containing 0.0808 g. (0.469 mmole) of N,N,N',N'-tetraethylethylenediamine. The tube was cooled in liquid nitrogen, evacuated and degassed, and 106.4 cc. (4.750 mmoles) of dimethylphosphine was then condensed in the tube. The sealed tube was heated in an oven at $200 \pm 15^\circ\text{C}$. for 15 hrs. at the end of which time the evolved hydrogen was measured as 103.6 cc. (97.4%). Volatile material was removed by sublimation at 180°C . for 20 min. leaving 0.2186 g. (62.2%) of linear polymer, m.p. $161-63^\circ\text{C}$.

b. Methylethylphosphinoborine Polymer

The results of 17 pyrolyses are summarized in Table II but only Experiment 59 in which both yield (70.2%) and melting point ($119-22^\circ\text{C.}$) of the polymer are high is reported in detail.

By means of a micro-buret with a long capillary tip, 0.6352 g. (5.523 mmoles, 123.8 cc.) of triethylamine borane and 0.072 g. (0.71 mmoles, 15.9 cc.) of triethylamine were introduced (by volume) into a 40 ml. heavy-wall Pyrex tube. The tube was cooled in liquid nitrogen, evacuated and degassed, and 0.4101 g. (5.3905 mmoles, 120.88 cc.) of methylethylphosphine was then condensed into the tube. The sealed tube was heated in an oven at $190 \pm 15^\circ\text{C}$. for 15 hrs. At the end of this time the evolved hydrogen was measured and amounted to 121.4 cc. (100.5%). Volatile material was removed by sublimation at 180°C . for 20 min. and amounted to 0.7733 g. The nonvolatile translucent residue was removed from the tube in hot benzene solution. The benzene was mostly evaporated in a stream of nitrogen and the last traces were removed in high vacuum to leave 0.3329 g. (70.2%) of white translucent plastic polymer, m.p. $119-22^\circ\text{C}$. (micro hot stage) having an

infrared spectrum identical to that previously obtained.²² The molecular weight of the product was determined isopiesticly in benzene solution to be 1698, D.P. 19 using azobenzene as the standard.

c. Diethylphosphinoborine Polymer

The preparations were made following the procedure described above for the preparation of linear dimethyl- and methylethylphosphinoborine polymers except that the conditions varied as described below.

In the first experiment pyrolysis of 0.4270 g. (4.739 mmoles) of diethylphosphine and 0.70 ml. (4.831 mmoles) of triethylamine borane for 15 hrs. at $185 \pm 15^\circ\text{C}$. yielded 98.6% of the theoretical hydrogen and 0.2243 g. (46.4%) of linear polymer, m.p. $257-58^\circ\text{C}$.

In the second experiment pyrolysis of 0.3998 g. (4.437 mmoles) of diethylphosphine, 0.65 ml. (4.48 mmoles) of triethylamine borane and 0.0722 g. (0.714 mmoles) of triethylamine for 15 hrs. at $185 \pm 15^\circ\text{C}$. yielded 100.1% of the theoretical hydrogen and 0.1925 g. (42.5%) of linear polymer, m.p. $257-59^\circ\text{C}$.

d. Attempt to Form Linear Dimethylphosphinoborine Polymer from Cyclic Trimer by Pyrolysis in the Presence of Tertiary Amines

(1) Triethylamine

A sealed 10 ml. bomb tube containing 0.0800 g. (0.3609 mmole) of dimethylphosphinoborine trimer and 0.1141 g. (1.128 mmole) of triethylamine was heated for 0.5 hr. at $350 \pm 5^\circ\text{C}$. and then was cooled gradually over a 3.5 hr. period to room temperature. The starting trimer was recovered quantitatively by sublimation at 60°C .

(2) Triethylenediamine

A sealed 10 ml. heavy-wall bomb tube containing 0.1352 g. (0.6097 mmole) of dimethylphosphinoborine trimer and 0.5011 g. (4.467 mmoles) of triethylenediamine was heated at $196 \pm 15^\circ\text{C}$. for 24 hrs. The tube was cooled, opened and 1.76 cc. of hydrogen was collected. The contents of the tube were sublimed in high vacuum at 90°C . to give 0.5602 g. of volatile material and 0.0257 g. of white amorphous solid, m.p. ca. $333-45^\circ\text{C}$. (turns brown at 160°C .). The infrared spectrum showed no B-H absorption.

Two other pyrolyses of dimethylphosphinoborine trimer with triethylenediamine at about 350°C . for 0.5 hr. gave some unidentified decomposition products which were not linear dimethylphosphinoborine polymers.

In a control experiment, a sealed tube containing 0.711 g. (6.34 mmoles) of triethylenediamine was heated at $230 \pm 5^\circ\text{C}$. for 20 hrs. then inadvertently at about 360°C . for 0.5 hr. The tube contents were sublimed at $120-30^\circ\text{C}$. and left 0.0685 g. of cream colored residue, m.p. ca. $150-220^\circ\text{C}$. with decomposition. The infrared spectrum of this material is virtually identical with that of the material isolated when trimer was present above.

e. Attempt to Prepare
Methylallylphosphinoborine Polymer

The exothermic formation of methylallylphosphine borine was controlled by the slow introduction of 57.8 cc. (2.58 mmoles) of diborane into a 50 ml. centrifuge cone containing 0.4538 g. (5.151 mmoles) of methylallylphosphine maintained at -78°C . An infrared spectrum of the degassed adduct was immediately obtained and showed essentially no change in the intensity of the C=C stretching band at 6.1μ compared with the free base. After standing for 2.5 days at room temperature the viscosity of the liquid adduct had increased markedly and some colorless solid was observed. A substantial decrease in unsaturation was indicated by a considerable weakening of the C=C stretching band and the appearance of the $-\text{CH}_2-$ stretching band at 3.4μ . These changes in the infrared spectrum were more pronounced after an additional 7 days during which time the adduct had changed to a slightly tacky solid.

f. Attempt to Prepare
Dimethylphosphinodichloroborine Polymer

(1) Dehydrohalogenation of
Dimethylphosphine Trichloroborine

Into an 80 ml. bomb tube was condensed 0.5450 g. (5.386 mmoles) of triethylamine, 121.4 cc. (5.420 mmoles) of dimethylphosphine, 121.3 cc. (5.415 mmoles) of boron trichloride and 13.0 ml. of benzene. After 15.5 hrs. at room temperature the sealed tube was opened and volatiles removed. Addition of 10 ml. chloroform dissolved most of the solid. The chloroform suspension was washed with four 5 ml. portions of water to remove triethylammonium chloride. Analysis of the aqueous phase indicated 4.63 mmoles (86.0%) N, 5.00 mmoles (92.8%) Cl⁻ and 0.60 mmoles B. The organic phase was diluted to 80 ml. with additional chloroform, filtered hot to remove 0.0495 g. of insoluble material indicated by infrared to be predominately boric acid, concentrated to approximately 40 ml. and allowed to cool overnight without crystallization. Further concentration did not promote crystallization. The solution was therefore evaporated to dryness and the 0.8400 g. slightly yellow tacky residue was separated into the following fractions by fractional solution:

- (I) Benzene insoluble; 0.1462 g. colorless powder, apparently the triethylamine adduct of linear dimethylphosphinodichloroborine trimer, m.p. $172-74^{\circ}\text{C}$.; Anal. found: C, 25.90; H, 6.27; Cl, 39.0; Calcd. for $[(\text{CH}_3)_2\text{PBCl}_2]_3\text{N}(\text{C}_2\text{H}_5)_3$: C, 27.22; H, 6.28; Cl, 40.18; N, 2.65. Efforts to obtain an isopiestic molecular weight in CHCl_3 were unsuccessful due to the destruction of the azobenzene standard by some unknown material in the system.
- (II) Ethanol insoluble; 0.1277 g. colorless powder, apparently linear dimethylphosphinodichloroborine polymer, m.p. $171-76^{\circ}\text{C}$.; Anal. found: C, 15.40, 16.66, 15.71; H, 2.94, 4.45, 5.56; Calcd. for $[(\text{CH}_3)_2\text{PBCl}_2]_n$: C, 16.82; H, 4.24. Efforts to obtain an isopiestic molecular weight in benzene were again unsuccessful due to the destruction of the azobenzene standard.

(III) Methanol insoluble; 0.0834 g. colorless powder, apparently linear dimethylphosphinodichloroborine polymer, partial melt 146-49°C., clear melt 174-77°C.

(IV) Methanol-water insoluble; 0.1128 g. colorless solid combination of three fractions, apparently linear dimethylphosphinodichloroborine polymer, partial melt 146-49°C., clear melt 171-74°C.

Infrared spectra of fractions (II), (III) and (IV) were nearly identical and were quite similar to that of linear dimethylphosphinodichloroborine prepared by chlorination of linear dimethylphosphinoborine. No useful correlations could be drawn from the infrared spectrum of fraction (I).

(2) Pyrolysis of Trimethylphosphine Trichloroborine

A small quantity of trimethylphosphine trichloroborine was prepared in a 5 ml. tube from 25.5 cc. (1.14 mmoles) each of boron trichloride and trimethylphosphine. The tube was sealed and heated for 13 hrs. at 290°C. A very small amount (1.4 cc.) of unidentified volatile material was formed without noticeable change of the solid. Further heating for 20 hrs. at 350°C. had no effect. Finally, during 13 hrs. at 500°C., noticeable decomposition of the adduct occurred. The volatile pyrolysis products were separated into 52.2 cc. (2.33 mmoles) of methane, 0.5 cc. (0.02 mmole) of hydrogen and approximately 1 mmole of condensable material shown by infrared analysis to be principally boron trichloride with traces of dichloroborine and silicon tetrachloride. The nonvolatile black solid residue was extracted with chloroform from which only a white pyrophoric material (probably white phosphorus) was isolated.

g. Dimethylphosphinodichloroborine Polymer

To 1.7463 g. (23.63 mmoles) of linear dimethylphosphinoborine polymer (D.P. 80) and 30 ml. of carbon tetrachloride, contained in a nitrogen-filled 50 ml. 2-neck flask fitted with a condenser, nitrogen inlet and a solids addition flask, was added in 5 min. 3.11 g. (23.4 mmoles) of aluminum chloride. The flask contents were stirred by means of a glass covered magnetic stirring bar and the flask was cooled in an ice bath during addition of the aluminum chloride. The ice bath was removed and the flask warmed to room temperature with no obvious reaction occurring. After 50 min., the finely divided solid coagulated. The mixture was stirred overnight, then 17 ml. of carbon tetrachloride was added and the solid filtered and dried. The filtrate was evaporated to give 10 mg. of residue which was discarded. The solid was slurried cautiously with 40 ml. of 3N hydrochloric acid, filtered and then washed successively with three 15 ml. portions of water and five 10 ml. portions of acetone. The washings were done in a centrifuge cone because the solid clogged filter paper. The vacuum-dried colorless solid weighed 1.0256 g. (31.7%), m.p. 215-25°C. under nitrogen (m.p. > 360°C. in air). The infrared spectrum (KBr disc) showed a small B-H band.

The acetone washes were combined and evaporated to give 1.3537 g. (41.9%) of a slightly yellow, easily powdered brittle glass which shrinks at 71°C., partially melts at 75-81°C. and all melts at 117°C. with foaming. The infrared spectrum showed B-H and boric acid bands.

h. Reaction of Methylethylphosphinoborine
Polymer with Methyl Chloride--Aluminum Chloride

Into a 40 ml. Pyrex bomb tube containing 0.3111 g. (3.5388 mmoles) of methylethylphosphinoborine linear polymer and 0.4895 g. (3.674 mmoles) of aluminum chloride was condensed about 4 ml. of methyl chloride. The tube was sealed, allowed to stand overnight at room temperature, then opened and 88.2 cc. (55.6%) of methane was collected. The volatile materials were removed from the tube and the residue was dissolved in a mixture of chloroform and water. The chloroform layer was separated and the solvent evaporated to give 0.4804 g. of brittle solid, m.p. 70-75°C. An infrared spectrum in CCl_4 showed B-H bonds in the product. After standing several days the product weighed only 0.3495 g. and was no longer a solid.

In two other experiments on the same scale, 57.7 and 53.7% yields of the theoretical methane were produced and the products were a viscous syrup and a brittle solid, m.p. 70-75°C., respectively. The latter solid analyzed 38.3% Cl (calcd. for $\text{CH}_3(\text{C}_2\text{H}_5)\text{PBCl}_2$: Cl, 45.2%).

i. Solubilities of Methylethyl- and
Diethylphosphinoborine Polymers

Linear methylethylphosphinoborine polymer was tested qualitatively for solubility in various solvents by placing 5-10 mg. in a 3 inch test tube with 0.2-0.8 ml. of the solvent. The tube was stirred about 5 min. at room temperature to see if the polymer dissolved (+), if not, it was heated on a steam bath for about 5 min. If the polymer dissolved (+) then the tube was cooled to see if it reprecipitated. The results, summarized in Table III, suggest n-hexane to be best for reprecipitation of the polymer.

The procedure for testing the solubility of linear diethylphosphinoborine polymer was similar to that described above for linear methylethylphosphinoborine polymer. Tested as solvents for the polymer were benzene, toluene, ethylbenzene, xylene, anisole, ethyleneglycol dimethyl ether, naphthalene (above 80°C.), acetonitrile, *p*-cymene, dimethylsulfoxide, water, methanol, triethylamine, tetrahydrofuran, dioxane, trimethylphosphine (sealed tube), hydrogen cyanide (sealed tube), dimethylphosphinoborine trimer (above 87°C.), and methylethylphosphinoborine trimer. The polymer was insoluble in all the above solvents except naphthalene at its boiling point (218°C.). Cooling the naphthalene solution to ca. 100°C. did not cause the polymer to reprecipitate, presumably because of thermal depolymerization.

j. Attempt to Prepare Dimethyl-
phosphinodimethylborine Polymer

(1) Using Methyllithium

Into a tube which was sealed through a sintered glass disc to an 80 ml. glass bomb were condensed 1.2107 g. (11.96 mmoles) of triethylamine, 268.2 cc. (11.97 mmoles) of methylphosphine, 267.8 cc. (11.96 mmoles) of dimethylbromoborine and 20 ml. of degassed anhydrous diethyl ether. An immediate formation of a copious colorless precipitate was observed upon warming the sealed tube to room temperature. After standing for 123 hrs. the reaction mixture was filtered through the sintered disc into the receiver arm. The insoluble by-product

ammonium salts, which were washed several times by condensing the solvent back into the reaction arm, contained 10.51 mmoles N (87.8%) and 10.95 mmoles Br⁻ (91.6%). Solvent was distilled from the filtrate and the tube containing the polymeric methylphosphinodimethylborine residue was sealed to a 40 ml. bomb tube containing 13.0 ml. (12.08 mmoles) of 0.929N ethereal methyl lithium. The methyl lithium solution was washed onto the polymer and the mixture then allowed to stand at room temperature for 7.5 days. The tube was opened, 72.6 cc. (27.0%) of methane removed and 266.1 cc. (11.88 mmoles) of methyl bromide added. After standing overnight at room temperature the tube was opened and an additional 36.8 cc. (13.7%) of methane removed. The clear ethereal reaction mixture was washed with four 5 ml. portions of water. The water washes contained 11.28 mmoles (94.9%) Br⁻, 0.71 mmole B and 0.004 mmole P. The ether layer was evaporated to dryness and the colorless solid residue sublimed at 135°C. under high vacuum. Essentially all of the material was volatile at this temperature. The principal sublimate was 0.3822 g. (24%) of a crystalline solid identified by infrared as trimethylphosphine trimethylborine. A 0.092 g. quantity of a less volatile amorphous translucent solid was also obtained.

(2) Using Sodium Amide

Linear methylphosphinodimethylborine polymer was prepared as previously reported (vide supra) from 1.2166 g. (12.02 mmoles) of triethylamine, 268.0 cc. (11.96 mmoles) of methylphosphine and 266.0 cc. (11.88 mmoles) of dimethylbromoborine in 22 ml. of anhydrous diethyl ether. A water extract of the ether-insoluble salts contained 11.2 mmoles Br⁻ (94.3%) and 11.1 mmoles N (93.4%). The water-insoluble portion was benzene soluble and consisted of 0.1985 g. of a translucent somewhat tacky amorphous solid. The tube containing the polymer was sealed to a tube containing liquid ammonia and iron-free sodium amide formed by the uncatalyzed reaction of 12.01 g.-atoms sodium and ammonia during one year. The contents of the two arms were combined at room temperature and then cooled as soon as the polymer layer disappeared. The cooled tube was opened and following the removal of 0.8 cc. of methane a 267.2 cc. (11.93 mmoles) quantity of methyl bromide was added. A vigorous reaction occurred near -78°C. upon warming the tube. An additional 0.7 cc. of methane was removed and the materials volatile at room temperature transferred to the high vacuum system. The colorless powdery residue was dissolved in water and extracted with cyclohexane. The cyclohexane extract contained only 37 mg. of an unidentified tacky solid. The aqueous solution contained 11.7 mmoles Br⁻ (98.1%), 0.16 mmole P and 0.61 mmole N. A 0.2020 g. (29.9%) quantity of a slightly volatile crystalline solid, which was identified by infrared as aminodimethylborine trimer,⁷ was isolated by fractional condensation. The remaining volatile material was passed through anhydrous zinc sulfate to remove amines and then separated by fractional distillation into 3.8 cc. of trimethylphosphine, 63.8 cc. of dimethylphosphine and 28 cc. of methylphosphine.

2. Cyclic Phosphinoborine Polymers

a. Dimethylphosphinoborine Trimer and Tetramer from Dimethylphosphonium Chloride and Lithium Borohydride

A total of 0.1394 g. (6.397 mmoles, 143.4 cc.) of lithium borohydride was packed into two thin-walled glass tubes in a dry box. The tubes were placed in a nitrogen-filled 40 ml. glass bomb tube containing dimethylphosphonium chloride which had been prepared on the high vacuum line from 143.8 cc. (6.416 mmoles) of dimethylphosphine and 144.0 cc. (6.425 mmoles) of hydrogen chloride. The tube was degassed and 5.0 ml. of diethyl ether was condensed into the tube

at 78°C. The tube was sealed, warmed to room temperature, shaken vigorously to break up the thin-wall glass tubes, and allowed to remain overnight at room temperature. The tube was opened and 123.7 cc. (86.3%) of the theoretical hydrogen was collected. The ether was removed, the evacuated tube was resealed and heated at $198 \pm 15^\circ\text{C}$. for 16 hrs. The tube was opened and 129.0 cc. (90.0%) of the theoretical hydrogen was collected (105% based on the hydrogen evolved in the first step of the reaction). The volatile product was sublimed in high vacuum using a luminous flame heat source to give 0.3419 g. (72.3%) of trimer-tetramer mixture, the identity of which was established by infrared analysis.

b. Dimethylphosphinoborine Trimer by Dehydrohalogenation of Dimethylphosphine Chloroborine

Into an 80 ml. bomb tube containing dimethylphosphine borine, which was prepared from 64.97 cc. (2.90 mmoles) of dimethylphosphine and 32.50 cc. (1.45 mmoles) of diborane, was condensed 64.97 cc. (2.90 mmoles) of hydrogen chloride. The sealed tube was maintained at -78°C . for 1 hr. during which time hydrogen was slowly evolved. Formation of dimethylphosphine chloroborine was completed by heating the tube at 50°C . for 41 hrs. After removal of 67.20 cc. (103.4%) of hydrogen, 0.2951 g. (2.916 mmoles) of triethylamine and 10 ml. of degassed diethyl ether were condensed into the tube which then stood at room temperature for 136 hrs. By-product triethylammonium chloride was removed by filtration and washed with three 5 ml. portions of ether. These salts contained 1.90 mmoles (65.1%) N, 1.82 mmoles (62.3%) Cl and 0.20 mmoles B. The ethereal filtrate was evaporated to dryness leaving a colorless liquid residue.

Upon heating this residue under vacuum at 95°C ., 0.0251 g. (0.113 mmole, 11.7%) of crude dimethylphosphinoborine trimer was obtained and identified by infrared analysis after recrystallization from methanol. A total of 49 mg. of colorless viscous liquid distillate was also obtained. The 102 mg. of colorless viscous liquid residue showed B-H stretching at 4.2μ (m) and strong bands in the $10\text{--}11\mu$ region which were possibly due to the B-Cl bond.

c. Attempt to Prepare Dimethylphosphino-diethylborine Trimer by Dehydrohalogenation of Dimethylphosphine Diethylchloroborine

Into one of two 100 ml. tubes connected by a sintered glass disk was condensed 0.9145 g. (8.760 mmoles) of diethylchloroborine, 0.8832 g. (8.727 mmoles) of triethylamine, 196.4 cc. (8.768 mmoles) of dimethylphosphine and 20 ml. of degassed diethyl ether. The tube was then sealed and warmed to room temperature. After standing overnight a copious colorless precipitate had formed in the initially clear solution. After standing for 111 hrs. the solution was filtered through the sintered glass disk. The precipitate was washed four times by condensing the solvent into the reaction arm and refiltering the resultant slurry. Solvent was removed from the filtrate and the arm containing the 1.2960 g. residue was sealed from the balance of the equipment. The residue, which was predominately a viscous liquid that became glassy at -78°C ., was too soluble in methanol to effect recrystallization. Removal of the methanol left a predominately liquid residue which oiled from a mixed hexane-benzene-methanol solvent. Solvent was again removed and the residue fractionated under high vacuum. A 0.2649 g. quantity of a complex liquid mixture volatile at room temperature was collected at -10°C . Minor quantities of a liquid-solid mixture was removed upon slowly increasing the temperature to 130°C . Between 130°C . and 150°C ., 0.0624 g.

of a colorless solid sublimate (m.p. 218-25°C.) was obtained. Efforts to obtain the molecular weight of this material isopiesticly in chloroform and benzene were unsuccessful. When chloroform was employed a colorless solid precipitate formed in the azobenzene standard solution and the sample was not sufficiently soluble in benzene even at 90°C. Anal. calcd. for $[(CH_3)_2PB(C_2H_5)_2]_3$: C, 55.44; H, 12.41. Found: C, 48.44; H, 10.73. The ether insoluble ammonium salts contained 4.8 mmoles (55%) N and 4.39 mmoles (50.3%) Cl^- .

d. Dimethylphosphinoborine--1,3-Trimethylene-
P,P'-bis(methylphosphinoborine) Copolymer

The benzene soluble residue⁸ from Experiment 4, weighing 0.1334 g., was sublimed about 6 hrs. at 150°C. in high vacuum to give three zones of partially crystalline sublimate: most volatile, 0.0005 g.; intermediate, 0.0047 g.; and least volatile, 0.0043 g. The sublimation residue was sublimed at 240°C. for about 2 hrs. to give 0.0276 g. of volatile material which was combined with the two least volatile fractions from the 150°C. sublimation (combined volatiles = A). The residue from the 240°C. sublimation was stored.

In order to obtain more material, the combined 0.3156 g. benzene soluble residues,⁸ from Experiments 1-3, still containing material volatile at 130°C. were sublimed for 6 hrs. at 130°C. to remove this material (0.0893 g.). The residue was sublimed at 150-250°C. for about 8 hrs. to give three zones of sublimate: most volatile, 0.0057 g.; intermediate, 0.0176 g.; and least volatile, 0.0315 g. The latter two fractions were combined with A (0.0857 g. total) and the residue was stored.

The combined volatiles were fractionally sublimed at $150 \pm 5^\circ C$. to give three zones of sublimate: most volatile, 0.0025 g.; intermediate, 0.0540 g.; and least volatile, 0.0033 g. The most volatile fraction was stored and the least volatile fraction (0.0192 g.) was combined with the residue (B). The intermediate fraction was sublimed at $135 \pm 5^\circ C$. in 2 hrs. The temperature was lowered to $100 \pm 2^\circ C$. and the heating bath raised which caused some material (0.0068 g.) to sublime from the 135°C. zone. The remaining 135°C. zone (0.0230 g.) had m.p. 107-11°C. (uncorr.) and was recrystallized from methanol to give fine colorless needles, m.p. 115-19°C. (uncorr.). This material is possibly the previously isolated material⁸ of m.p. 121-22°C. A mixed melting point was not taken since none of the 121-22°C. material was available.

The residue from the 135°C. sublimation and B above were combined (total 0.0467 g.) and sublimed at 170°C. and then 190°C. but no clear fractionation occurred. The residue weighed 0.0275 g. and was stored. The sublimate (0.0167 g.) was again sublimed at $190 \pm 5^\circ C$. then the temperature was lowered to $170 \pm 10^\circ C$. and the heating bath raised to encompass the volatile material which had collected above the 190°C. bath level. This procedure caused two zones to separate and left a small amount of residue (0.0039 g.). The 170°C. and 190°C. zones (most volatile and least volatile, respectively) were mechanically separated. The 170°C. (0.0028 g.) and 190°C. (0.0093 g.) materials were both recrystallized from methanol to give 0.0008 g. and 0.0032 g. of colorless needles, respectively. All of the isolated materials were stored since they were insufficient for meaningful analyses.

e. Reaction of Dimethylphosphinoborine Trimer with Cyanogen Bromide

In a high vacuum line experiment, 0.5231 g. (4.938 mmoles) of cyanogen bromide was condensed into a 10 ml. heavy-wall tube containing 0.1853 g. (0.8357 mmole) of dimethylphosphinoborine trimer and about 2 ml. of cyclohexane (dried over P_4O_{10}). The tube was sealed and shaken. The solids dissolved and a second liquid phase appeared. The tube was heated at $100 \pm 3^\circ C.$ for 15 hrs., cooled and opened to the vacuum line. A total of 1.95 cc. of permanent gas (probably hydrogen) and 77.6 cc. of a mixture of condensable gases, which appeared to be mainly hydrogen cyanide, were isolated. The solid in the tube was subjected to vacuum sublimation at $60^\circ C.$ but only a trace (ca. 1-5 mg.) of volatile material was obtained. The residue amounted to 0.4186 g., and starts to melt with shrinking at $105^\circ C.$ and all melts at $150^\circ C.$ (Anal. calcd. for $C_6H_{21}P_3B_3Br_3$: Br, 52.3. Found: Br, 57.2). The infrared spectrum of the product is almost identical to that of dimethylphosphinobromoborine trimer.

In another experiment which used 0.2359 g. (2.227 mmoles) of cyanogen bromide, 0.4919 g. (2.218 mmoles) of trimer and 3.5 ml. of cyclohexane, 98.5% of the starting trimer was recovered after an 18 hr. reaction period at room temperature.

f. Attempt to React Dimethylphosphinoborine Trimer with Cyanogen

In addition to the preparation of cyanogen, five separate high vacuum line experiments were performed in an attempt to introduce cyano groups into the dimethylphosphinoborine molecule. The procedures were all very similar and consequently only experiment 1 is described in detail while only quantities of reactants and a brief description of conditions are outlined for experiments 2-5.

(1) Cyanogen

Ten grams (74.4 mmoles) of silver cyanide were heated at $310^\circ C.$ (54.8% potassium nitrate - 45.2% sodium nitrate bath) for 3 hrs. The gas evolved during this period was discarded. The bath temperature was raised to $350-75^\circ C.$ for 4 hrs. The evolved gas was passed over glass beads, coated with phosphorus pentoxide and collected in a $-196^\circ C.$ trap. The product was purified by successive passage through $-78^\circ C.$, $-112^\circ C.$ and $-196^\circ C.$ traps. The material retained in the $-112^\circ C.$ trap was pure cyanogen as indicated by its infrared spectrum, vapor tension at $-22.8^\circ C.$ (700 mm.) (Lit.¹⁰, -701.6 mm.), and vapor density molecular weight determination of 51.9 (calcd. 52.04). The product was stored in a stainless steel cylinder and amounted to 1.6 g. (30.7 mmoles, 82.5%).

(2) Attempted Cyanogenation

Experiment 1. Into a 10 ml. heavy-wall bomb tube containing 0.1120 g. (0.5051 mmole) of dimethylphosphinoborine trimer was condensed 68.6 cc. (3.061 mmoles) of cyanogen. The tube was sealed and heated at $80 \pm 1^\circ C.$ for 16.5 hrs. after which the solution was clear and colorless except for a thin film of brown material on the walls of the tube. Upon cooling to $-196^\circ C.$ and rewarming to room temperature, colorless crystals were present. The trimer did not dissolve entirely in mixture before heating. The tube was opened and found to contain no noncondensable gas. The condensable gas amounted to 69.0 cc. (100.6% recovery) in which no hydrogen cyanide could be detected by fractionation through a $-85 \pm 5^\circ C.$

trap. (In experiments 2-5, infrared spectroscopy was used to detect hydrogen cyanide.) The residue was sublimed in high vacuum at 60-70°C. to give the starting trimer, m.p. 86-87°C. (uncorr.). The amount of trimer recovered was not determined.

Experiment 2. The reactants were 0.1496 g. (0.6747 mmole) of trimer, 0.1153 g. (0.9819 mmole) of zinc cyanide (dried 1 hr. at 100°C. in high vacuum) and 91.5 cc. (4.082 mmoles) of cyanogen. The tube was heated at 60 ± 1°C. for 8 hrs., 180 ± 2°C. for 17 hrs. and 200 ± 10°C. for 16 hrs. The first heating resulted in formation of a trace of HCN, the second about 3% and the third about 9% as estimated from infrared spectra. Sublimation of the residue gave 0.0967 g. of pure and 0.0195 g. of impure trimer. The presence of -CN group could not be detected in the infrared spectrum of the impure trimer.

Experiment 3. The reactants were 0.0974 g. (0.4393 mmole) of trimer and 60.0 cc. (2.677 mmoles) of cyanogen. The tube was heated at 100°C. for 8 hrs., 180 ± 2°C. for 17 hrs. and 200 ± 10°C. for 16 hrs. The first heating resulted in formation of a trace of HCN, the second about 4% and the third about 9% as estimated from infrared spectra. Sublimation of the residue gave 0.0822 g. of pure trimer, 0.0064 g. of colorless amorphous material which softened at about 90°C. and was all melted at 105°C., and 0.0011 g. of crystalline material, m.p. 103-7°C.

Experiment 4. The reactants were 0.1212 g. (0.5466 mmole) of trimer, 0.0077 g. (0.032 mmole) of benzoyl peroxide and 57.1 cc. (2.548 mmoles) of cyanogen. The tube was heated at 90 ± 2°C. for 5 hrs. A small undetermined amount of HCN was formed and sublimation of the residue yielded 0.1127 g. of a mixture which was mainly starting trimer composed of a brittle glass and colorless crystals, m.p. 83-87°C.

Experiment 5. The reactants were 0.1149 g. (0.5182 mmole) of trimer, 0.1389 g. (2.185 g.-atoms) of copper powder and 51.5 cc. (2.298 mmoles) of cyanogen. The tube was heated at 90 ± 2°C. for 9 hrs. and at about 130°C. for 4 hrs. forming only a trace of HCN. Sublimation of the residue gave 0.1142 g. of trimer, m.p. 87.5-88.5°C.

g. Dimethylphosphino-
difluoroborine Trimer

A 1.000 g. (4.51 mmoles) quantity of dimethylphosphinoborine trimer was dissolved in 10 ml. of anhydrous hydrogen fluoride contained in a polyethylene bottle at -78°C. and allowed to warm slowly to room temperature in the hood. A viscous brown oil remained after 3 hrs. The remainder of the volatile material was removed at aspirator pressure whereupon 1.210 g. (81%) of crude crystalline product formed, m.p. 127-29°C. An analytical sample was prepared by recrystallization from methylcyclohexane and sublimation at 80-85°C. (10⁻⁴ mm.), m.p. 129-30°C. Calculated for $[(CH_3)_2PBF_2]_3$: C, 21.87; H, 5.50. Found: C, 21.92; H, 5.65.

The experiment was repeated on a larger scale using 4.000 g. (18.0 mmoles) of dimethylphosphinoborine trimer and 27 ml. of hydrogen fluoride. The crude product, weighing 5.8554 g. was obtained in 98% yield, m.p. 127-28°C. After purification 5.0002 g. (84%) of pure product, m.p. 129-30°C. was isolated.

A third experiment was performed in order to determine the stoichiometry of the fluorination reaction, by measuring the hydrogen evolution.

To 0.1054 g. (0.4755 mmole) of dimethylphosphinoborine trimer in a 10 ml. stainless steel cylinder connected to the vacuum line was condensed approximately 2 ml. of hydrogen fluoride. The cylinder was warmed slowly to room temperature and allowed to stand for 5 days with occasional shaking. The 65.98 cc. of hydrogen which had formed corresponded to 6.19 moles per mole dimethylphosphinoborine trimer (theoretical, 6.00).

B. Evaluation of Phosphinoborines

1. Thermal Stability of Dimethylphosphinodichloroborine Trimer

Three sealed melting point tubes containing small samples of dimethylphosphinodichloroborine (m.p. 381-83°C.) were placed in a refluxing mercury bath at 357°C. After 1 hr., a tube was withdrawn and found to be slightly discolored with m.p. below 365°C. After 2 hrs. a second tube was withdrawn and was more discolored (yellow) than the first tube. The melting point was below 295°C. After 2.5 hrs. the third tube was withdrawn and was deep orange in color. It exploded at 302°C. without first melting.

C. Organophosphines

1. Methylallylphosphine

Methylallylphosphine was prepared from 5.3 g. (0.23 mole) of sodium, 15.9 g. (0.33 mole) methylphosphine and 18.6 g. (0.24 mole) allyl chloride in liquid ammonia, as previously described¹² except that the crude product was separated from the reaction mixture by azeotropic distillation. The product, $\text{CH}_3(\text{CH}_2=\text{CHCH}_2)\text{PH}$, 4.61 g. (0.052 mole) was obtained in 22.5% yield on fractional distillation of the crude material at -38°C. A new series of vapor tensions determine the equation $\log_{10} p_{\text{mm.}} = 7.934 - 1785.7/T$ from which the boiling point is calculated to be 80.9°C. The molecular weight was determined by vapor density to be 87.5 (calcd. 88.09).

2. 3,3-Dimethylcyclotrimethylenephosphine

a. Halide Synthesis

A 557.79 g. (2.06 moles) quantity of phosphorus tribromide was added over a 1.5 hr. period to 214.2 g. (2.06 moles) of neopentyl glycol in 135 ml. of benzene at 70-80°C. using good mechanical agitation. The evolved HBr was discarded and the mixture was then refluxed for 20 hrs. The benzene was stripped off over a 1 hr. period and the remaining mixture was refluxed at 147°C. for 18 hrs. Ice (250 g.) was added and the mixture stirred slowly for 30 min. The product was then steam distilled over a 4 hr. period. The organic distillate was dried over potassium carbonate, filtered and the filter cake washed with 50 ml. of n-pentane. The product was distilled through a spinning band column, b.p. 72-73°C. at 20 mm. to give 122.1 g. (0.521 mole; 25.3% yield) assaying 98.1% by vapor phase chromatography.

b. Phosphine Synthesis

In a preliminary solubility test a mixture of about 5 ml. of ammonia and 0.5 ml. 1,3-dibromo-2,2-dimethylpropane sealed in a glass tube was

observed to become homogeneous near 0°C. Sodium phosphinide, prepared from 382.0 cc. (17.05 mmoles) of phosphine and 0.3837 g. (16.69 mmoles) of sodium dissolved in 10 ml. of liquid ammonia contained in a 180 ml. glass bomb tube, was allowed to react at room temperature for 3 weeks with 1.922 g. (8.358 mmoles) of 1,3-dibromo-2,2-dimethylpropane. The bomb tube was opened and the crude product and ammonia fractionally condensed in a -135°C. trap. The more volatile material which was condensed in a -196°C. trap, was found to be phosphine but was not measured due to mechanical loss. The crude product was transferred into a modified centrifuge cone and the lower liquid layer (at -78°C.) was mechanically separated from the ammonia. After standing at room temperature under a nitrogen atmosphere for 24 hrs., the product had polymerized to a clear, very viscous liquid with no detectable vapor pressure at room temperature. An infrared spectrum of the liquid was obtained for reference purposes.

A second experiment following the same general procedure was performed using 411.5 cc. (18.37 mmoles) of phosphine, 0.4118 g. (17.91 mmoles) of sodium, and 2.101 g. (9.136 mmoles) of 1,3-dibromo-2,2-dimethylpropane in 10 ml. of ammonia. The reaction time was shortened to 10 min. at -78°C. The products obtained were 153.6 cc. (6.86 mmoles) of phosphine and an undetermined amount of a volatile organophosphine tentatively characterized as 3,3-dimethylcyclotrimethylenephosphine by infrared analysis and a vapor density molecular weight of 92.8 (calcd. for $C_5H_{11}P$, 102.12). A series of vapor tensions determine the equation $\log_{10} p_{\text{mm.}} = 5.545 - 1235/T$ from which are calculated the doubtful values, boiling point 190°C., $\Delta H_v = 5.65$ kcal./mole, and Trouton constant = 12.2 e.u.

3. Diethylphosphine from Tetraethylbiphosphine Disulfide

a. Tetraethylbiphosphine Disulfide

To a 3-l. flask fitted with reflux condenser, stirrer, addition funnel and thermometer was added 500 ml. 3M (1.5 moles) ethylmagnesium bromide diluted with 500 ml. of ether. Dropwise addition of a solution of 86.0 g. (0.5 mole) thiophosphoryl chloride in 120 ml. of ether resulted in the formation of a thick slurry after about two-thirds of the solution was added. The mixture was refluxed for 1 hr. on a steam bath, cooled and 10% sulfuric acid (600 ml.) added until two clear layers were obtained. The ether layer was separated, dried with 20 g. of sodium sulfate and the ether distilled off. The crystalline residue was washed with 100 ml. of methanol, filtered, recrystallized from aqueous acetone and dried under high vacuum. Tetraethylbiphosphine disulfide $[(C_2H_5)_2PS]_2$, m.p. 75-76°C., weighing 21.3 g. (0.088 mole), was isolated in 35.2% yield. An additional 6.7 g. (0.027 mole) of product, m.p. 74-76°C., was recovered from the wash and mother liquors, giving a total yield of 46.0%.

In a larger second preparation, tetraethylbiphosphine disulfide was made by dropwise addition of a solution of 76.0 g. (1.04 moles) of thiophosphoryl chloride in 240 ml. of diethyl ether to 1000 ml. (3 moles) of ethylmagnesium bromide diluted with 1000 ml. of ether. The crude semi-solid product was isolated from the ethereal solution and an attempt to recrystallize from an aqueous-acetone solution without a preliminary methanol wash produced an insoluble oil. The two-phase solution was extracted with ether and the extract was dried and stripped of solvent. The resulting solids were washed with 100 ml. of cold methanol, filtered and recrystallized from an aqueous-acetone solution to yield 22.4 g. (0.099 mole) tetraethylbiphosphine disulfide, $[(C_2H_5)_2PS]_2$, m.p. 68.5-

70.5°C. An additional 11.6 g. (0.05 mole) of solid, m.p. 62-66°C. were recovered from the wash liquor on evaporation inadvertently done in an oxygen atmosphere giving a total yield of 28.1% along with a significant quantity of oily liquids.

b. Diethylphosphine from
Isolated Disulfide

To a nitrogen-flushed, 4-neck, 1-l. Morton flask fitted with stirrer, reflux condenser, addition funnel and gas inlet tube was added a slurry of 20 g. (0.083 mole) of tetraethylbiphosphine disulfide in 100 ml. of ether. Addition of an excess of lithium aluminum hydride by Soxhlet extraction and as an ethereal solution resulted in the formation of white insoluble solid. The reaction slurry was refluxed for 50 min., cooled, 100 ml. of ether added, and 250 ml. water added dropwise, until a clear ether layer was obtained. The ether layer was removed by pressure siphon under nitrogen and the solids washed with 225 ml. of ether and 125 ml. of water. The combined ether layers were filtered, dried with 60 g. of sodium sulfate and refiltered under nitrogen. Using a 200 mm. Helipac column flushed with nitrogen and vented through a mercury bubbler the ether was distilled off leaving a clear yellow liquid residue which was distilled into a -78°C. trap under reduced pressure and subsequently transferred to the vacuum line. The product, isolated in 27.7% yield by fractional condensation, and identified as diethylphosphine by infrared analysis and vapor pressures, weighed 4.141 g. (0.046 mole).

c. Diethylphosphine from
Disulfide Reaction Mixture

In the same manner (vide supra) another preparation of tetraethylbiphosphine disulfide was made to evaluate preparation of diethylphosphine without isolation of the intermediate disulfide. The slurry produced by the addition of 254.5 g. (1.5 moles) thiophosphoryl chloride in 360 ml. of ether to 1500 ml. (4.5 moles) ethylmagnesium bromide in 2000 ml. of ether was divided into two approximately equal portions by pressure siphoning the reaction slurry into two nitrogen-filled, 5000 ml. flasks.

(1) Reduction of the Hydrolyzed Portion

One portion was hydrolyzed using 600 ml. of 10% sulfuric acid. The dried ethereal solution containing the tetraethylbiphosphine disulfide was then reduced using 500 ml. of a freshly prepared 1.57M ethereal solution of lithium aluminum hydride. The ether was stripped from the dry solution and the remaining higher boiling liquids subjected to fractional distillation. However, inadvertent use of oxygen instead of nitrogen for the column atmosphere resulted in appreciable oxidation and loss of product.

(2) Direct Reduction of the Slurry

The second portion was reduced using the same equipment as previously described, by the dropwise addition of 500 ml. of ethereal 1.56M lithium aluminum hydride, followed by refluxing for 8 hrs. After 500 ml. of water was added the ethereal layer was removed by pressure siphon, dried over NaSO₄ and concentrated by distillation. Fractionation of residual material gave 20.2 g. (0.224 moles, 30% yield) in three cuts assaying vapor chromatographically as follows: 8 g. (85%), b.p. 61-70°C.; 9 g. (90%), b.p. 81-7°C.; 17.5 g. (30%), b.p. 127-40°C.

4. Cycloethylenephosphine

Employing the original synthetic procedure,⁵ sodium phosphinide, prepared from 1533 cc. (68.42 mmoles) of phosphine and 1.56 g. (67.9 mmoles) of sodium dissolved in 17 ml. of liquid ammonia and contained in a 190 ml. glass bomb tube, was allowed to react with 3.3619 g. (33.97 mmoles) of ethylene chloride at $-55 \pm 25^\circ\text{C}$. After being warmed momentarily to room temperature the phosphine layer was separated in a modified 50 ml. centrifuge cone. The crude product was purified by passage through anhydrous zinc sulfate at 0°C . followed by fractional condensation through a -100°C . trap. The vapor tension curve and infrared spectrum of the purified material (1.503 g., 74%) were identical with those previously observed.⁵

5. Dimethylphenylphosphine

A mixture of 2785 ml. of 3.2M (8.94 moles) of methylmagnesium bromide and additional methylmagnesium bromide, prepared from 58.7 g. (2.42 moles) of Mg and a solution of 230 g. (2.42 moles) of CH_3Br in 700 ml. of anhydrous diethyl ether, was cooled to 0°C . and 940 g. (5.25 moles) of phenyldichlorophosphine was added dropwise with stirring during 3 hrs. The reaction mixture was refluxed for 1 hr. and then recooled to below 0°C . before adding a total of 700 ml. of saturated aqueous ammonium chloride and 2000 ml. of degassed water to the mixture. The slightly yellow ether layer was separated and dried over 250 g. of anhydrous sodium sulfate.

The dried ether solution was concentrated and fractionally distilled to obtain the following fractions:

<u>Fraction</u>	<u>Weight, g.</u>	<u>b.p., $^\circ\text{C}$. at 40 mm.</u>
1	15.6	94-100
2	326.8	100-101

The dimethylphenylphosphine (Fraction 2, 2.37 moles) was obtained in 45.1% yield.

6. Attempt to Prepare p-Dimethylphosphinophenyldichlorophosphine

Into a 2000 ml. 3-neck flask equipped with a dropping funnel, thermometer, Hershberg stirrer and a reflux condenser was placed 303 g. (2.2 moles) of phosphorus trichloride. Slow addition of 42.5 g. (0.31 mole) of dimethylphenylphosphine was accompanied by evolution of hydrogen chloride. Excess phosphorus trichloride was removed by the addition of 300 ml. of toluene followed by distillation of the mixture until pure toluene distilled (109°C .). The product was used in this crude form for subsequent experiments.

In a second preparation an excess of hydrogen chloride was added to 41.5 g. (0.3 mole) of dimethylphenylphosphine in 400 ml. of ether to give 14.1 g. (0.088 mole) of solid monohydrochloride and 22.8 g. (0.108 mole) of liquid dihydrochloride. To the mixed hydrochlorides, contained in a 1000 ml. 3-neck flask fitted with a condenser, dropping funnel and Hershberg stirrer, was added dropwise 140 ml. (220 g., 1.6 moles) of phosphorus trichloride. No measurable evolution of hydrogen chloride was observed. The dropping funnel was replaced with a large rubber tube

leading to a flask containing 80.5 g. (0.6 mole) of aluminum chloride. Addition of the aluminum chloride resulted in rapid evolution of hydrogen chloride and the solution turned a bright orange color. After heating the mixture under reflux for 1 hr., 39 ml. (65.4 g., 0.425 mole) of phosphorus oxychloride was added slowly with the formation of a precipitate of phosphorus oxychloride-aluminum chloride complex. The solvent was removed from the ether soluble material by distillation through a 6 in. Vigreux column leaving a black viscous residue from which very little material distilled.

7. Attempt to Prepare
p-Bis(dimethylphosphino)benzene

To the bright orange toluene solution of what was presumed to be p-dimethylphosphinophenyldichlorophosphine (experiment 1, section 6; vide supra) was added 250 ml. of ether followed by 223 ml. of 3.2M (0.71 mole) methylmagnesium bromide while maintaining the flask at 0°C. by external cooling. After heating under reflux for 1.5 hrs. and cooling to 0°C., 500 ml. of aqueous saturated ammonium chloride solution was added. The aqueous layer was separated, and extracted exhaustively with ether. The combined ethereal solution was dried over sodium sulfate and concentrated by distillation. Distillation through a 6 in. Vigreux column yielded some dimethylphenylphosphine, while the major portion of the mixture remained in the flask without distilling up to 92°C. (30 mm.) and solidified to a dark brown mass. Attempts to obtain a pure material from the residue by crystallization from either toluene or ether were unsuccessful.

8. Attempt to Prepare
p-Dimethylphosphinophenylphosphine

An attempt to prepare p-dimethylphosphinophenylphosphine was made by the addition of the black viscous material presumed to contain p-dimethylphosphinodichlorophosphine (experiment 2, section 6; vide supra) in 250 ml. of anhydrous ethylene glycol dimethyl ether to a slurry of 10.0 g. (0.27 mole) of lithium aluminum hydride in 500 ml. of the same solvent. Excess reagent was decomposed by the slow addition of 500 ml. of water. The ether layer was separated and the residue thoroughly extracted with benzene. After drying the combined organic materials over sodium sulfate and removal of the solvents, a dark brown viscous residue remained. A white solid sublimate, obtained from the residue, appeared to decompose when an attempt was made to sample the material for an infrared analysis which was uninterpretable.

9. Attempt to Prepare
Dimethylaminodiethynylphosphine

a. Sodium Acetylide Method

To a slurry of 26.9 g. (0.58 mole) of freshly prepared sodium acetylide²³ in 300 ml. of ether contained in a 3-neck, round-bottom flask fitted with stirrer, Dry Ice condenser and addition funnel, was added dropwise, a solution of 46.7 g. (0.32 mole) of dimethylaminodichlorophosphine in 30 ml. of ether. No noticeable reaction occurred and upon filtration and distillation of the reaction slurry the starting materials were recovered.

b. Ethynylmagnesium Bromide Method

A solution containing approximately 18% ethynylmagnesium bromide and 82% methylmagnesium bromide was prepared by passing acetylene through a -78°C . trap into 280 ml. of 3M methylmagnesium bromide diluted with 200 ml. of ether for 3 hrs. at 1 atmosphere and 4 hrs. at 1.5 atmospheres.²⁴

Using the same apparatus described above, the Grignard solution (240 ml.) was added, dropwise, to a solution of 62.5 g. (0.43 mole) of dimethylaminodichlorophosphine in 400 ml. of ether at -78°C . and a white flocculent solid was formed. After standing for 1 hr. at -78°C . a small amount of black tar, which became the major insoluble constituent upon warming to room temperature, was observed. The ether solution was separated by filtration and the tar washed with 200 ml. of ether. Solvent was removed from the ether solution using a Vigreux column. The distillation residue consisted of a small amount of black solid tar and approximately 10 ml. of a slightly viscous yellow liquid. High vacuum fractional distillation of the volatile constituents yielded three fractions. Infrared analysis identified the most volatile (532 mm. at 24.0°C .) as diethyl ether and the least (1-2 mm. at 26.0°C .) to be primarily bis(dimethylamino)chlorophosphine. The intermediate fraction (12-18 mm. at 22.0°C .) had a P-N band in the infrared spectrum but was not further identified.

A previous attempt to prepare a concentrated solution of ethynylmagnesium bromide from ethylmagnesium bromide²⁴ failed due to the instability of the compound on storage.

10. Bis(dimethylamino)methylphosphine

The intermediate bis(dimethylamino)chlorophosphine was prepared in 60.7% yield according to the procedure previously described²⁵ from 510 g. (3.71 moles) of phosphorus trichloride in 5400 ml. of diethyl ether and 675 g. (15.0 moles) of anhydrous dimethylamine.

In a 12-l., 3-necked flask equipped with a Hershberg stirrer, condenser and dropping funnel vented through a mercury bubbler was placed 5500 ml. of diethyl ether and 570.6 g. (3.69 moles) of bis(dimethylamino)chlorophosphine. The flask was externally cooled to -70°C . and 610 ml. of 3M methylmagnesium bromide diluted with 390 ml. of ether was added dropwise in two portions over a period of 5 hrs., followed by the addition of 600 ml. of ether. Then 630 ml. of 3M methylmagnesium bromide, diluted with 320 ml. of ether, was added over a period of 2 hrs. A total of 2.7 moles of Grignard reagent was employed, whereafter the mixture was allowed to stand overnight at -70°C . The mixture was then warmed to room temperature and pressure filtered under nitrogen. The precipitate was washed with three 500 ml. portions of ether; the ether extracts were added to the filtrate and concentrated by distillation through a 12 in. Vigreux column. Bis(dimethylamino)methylphosphine, 169.7 g. (1.27 moles, 34.4%), was obtained by reduced pressure fractional distillation of the concentrate, b.p. $64-67^{\circ}\text{C}/49-50$ mm.

11. Methyldichlorophosphine

To a well-stirred solution of 169.7 g. (1.27 moles) of bis(dimethylamino)methylphosphine in 2000 ml. of ether, contained in a 5-l., 3-necked flask cooled externally in an ice-bath and equipped with a nitrogen inlet tube, Hershberg stirrer and condenser vented through a mercury bubbler, was added

184 g. (5.05 moles) of anhydrous hydrogen chloride over a period of 6.5 hrs. After the addition of 500 ml. of ether to the viscous reaction mixture, it was filtered under nitrogen and the precipitate was washed with 1500 ml. of ether. The ethereal solution was concentrated by distillation through a 12 in. Vigreux column in a nitrogen atmosphere. The residue was distilled through a 40 cm. tantalum spiral column; methyldichlorophosphine, 64.5 g. (43%) was collected at a boiling point of 80-81°C.

12. Attempt to Prepare Methyl-
(chloromethyl)chlorophosphine

To a solution of 5.9 g. (50.4 mmoles) of methyldichlorophosphine and 40 ml. of diethyl ether, contained in a 500 ml. 3-necked flask which was fitted with a dropping funnel, nitrogen inlet and Teflon covered magnetic stirring bar and cooled externally to -65°C. was added dropwise during 1 hr. 133 ml. of 0.41M (55.1 mmoles) of diazomethane prepared from N-methyl-N-nitroso-p-toluenesulfonamide.²⁶ A white precipitate formed upon addition of the first few drops which increased in quantity as the diazomethane was added. After the addition the mixture was allowed to warm slowly and stand at room temperature overnight. The contents of the flask were filtered under nitrogen and the filtrate concentrated by distillation of the ether through a 12 in. Vigreux column. An infrared analysis of the residue indicated that this material was mainly methyldichlorophosphine and ether containing a very small amount of a material which could be the desired methyl(chloromethyl)-chlorophosphine as suggested by a weak absorption band at 744 cm.⁻¹ indicative of the C-Cl bond.

The white precipitate formed from the reaction was soluble in water and became a light yellow viscous liquid when exposed to air, suggesting that the material is a complex polyphosphonium salt.

13. Organobromine Intermediates

a. o-Bromobenzyl Bromide

A 360.0 ml. (6.595 moles) quantity of bromide was added to 1057.5 g. (6.140 moles) of refluxing o-bromotoluene (99.3%) during 2 hrs. in a light catalyzed reaction using a 150 watt light bulb. The mixture was refluxed an additional 1.5 hrs., cooled, and distilled from the tar under reduced pressure (b.p. 125°C./12 mm.). The distillate was found to react with stainless steel and was fractionated using a 62 cm. tantalum spinning band column to give 941.8 g. (6.768 moles) of purified material, b.p. 128-30°C./20 mm., assaying 99.8% as determined by vapor phase chromatography; yield, 61.4%.

b. o-Bromobenzyl Methyl Ether

A 77.2 g. (0.296 mole) quantity of o-bromobenzyl bromide was added to 99.0 g. (3.09 moles) of refluxing methanol containing 17.88 g. (0.447 mole) of sodium hydroxide during 2 hrs. After 42 g. of methanol was stripped from the mixture 200 ml. of distilled water was added, the organic phase removed, washed twice more with distilled water, and then dried over potassium carbonate. The filtrate was fractionated through a small Vigreux column at 13 mm. The product was collected in two fractions (89-93°C. and 93-99°C.). The fractions were distilled on a spinning band column to give 42.6 g. (0.211 mole) of o-bromobenzyl methyl ether, b.p. 55-56°C. at 3 mm.; yield 71.3% assaying 99.5% by vapor phase chromatography.

D. Borines

1. Methyldibromoborine

Into an 80 ml. glass bomb tube were condensed 7.224 g. (28.83 mmoles) of boron tribromide and 313.1 cc. (13.98 mmoles) of trimethylborine. The sealed tube was heated at 152°C. for 40 hrs. Fractional distillation of the reaction mixture yielded traces of trimethylborine, 364.3 cc. (16.26 mmoles) of dimethylbromoborine, 3.8054 g. (15.19 mmoles) of boron tribromide and 1.5545 g. (8.37 mmoles, 20.0%) of methyldibromoborine (v.t. 4.0 mm./-45.2°C.).

E. Borazenes

1. N-Dimethyl-B-Trimethylborazene

a. Pyrolysis Method

Into an 80 ml. glass bomb tube equipped with two seal-off tips were condensed 449.5 cc. (20.07 mmoles) of methylamine, 223.7 cc. (10.00 mmoles) of ammonia and 670.2 cc. (29.92 mmoles) of trimethylborine. Pyrolysis of the liquid mixture of borine adducts at 350°C. for 2 hrs. and at 380°C. for 3.5 hrs. produced 1202 cc. (53.66 mmoles, 89.7%) of methane. Pyrolysis for an additional 6 hrs. at 360-80°C. increased the amount of methane to 1273 cc. (56.83 mmoles, 95.0%). Volatile products were transferred to the high vacuum system and separated by fractional condensation into the following components:

- (I) Methylaminodimethylborine contaminated with dimethylaminodimethylborine; 48.4 cc., passed a -63.5°C. cold trap. Infrared analysis showed N-H stretching at 2.89μ (w), a typical B-N band at 6.6μ (s) and weak bands at 6.85μ , 8.3μ , 9.0μ and 10.15μ due to dimethylaminodimethylborine.
- (II) Dimethylaminodimethylborine; 24.7 cc.; passed a -45.2°C. cold trap, stopped by a -63.5°C. cold trap. The following vapor tensions were observed at -45.2°C., -22.8°C. and 0°C., respectively, 2.8 mm., 13.9 mm., and 54.0 mm. in agreement with the literature²⁷ values 2.76 mm., 14.2 mm. and 52.6 mm., respectively. The infrared spectrum contained the typical B-N band at 6.6μ (s).
- (III) Crude B-trimethylborazene, 0.0835 g. (0.681 mmole, 6.8%); passed a -30.7°C. cold trap, stopped by a -45.2°C. cold trap. Observed vapor tension 9.8 mm./25.5°C.; reported for B-trimethylborazene 12.7 mm./25.0°C.²⁸
- (IV) N-methyl-B,B',B''-trimethylborazene, 0.3880 g. (2.84 mmoles, 28.5%); passed a -22.8°C. cold trap, stopped by a -30.7°C. cold trap. Observed vapor tension 3.2 mm./25°C. reported for N-methyl-B,B',B''-trimethylborazene 3.3 mm./25°C.²⁹
- (V) N,N'-dimethyl-B,B',B''-trimethylborazene, 0.5446 g. (3.68 mmoles, 36.2%); passed 5°C. cold trap, stopped by a -5°C. cold trap; observed vapor tension 1 mm./25°C. The infrared spectrum showed a band at 2.92μ (w) due to N-H stretching and B-N ring oscillation band at 6.8μ (vs).

- (VI) Crude hexamethylborazene, 0.0445 g. (0.270 mmoles, 2.7%); stopped by a 5°C. cold trap. Melting point 87-91°C., reported for hexamethylborazene 97.1°C.¹⁵

A 0.1779 g. quantity of unidentified solid sublimate was obtained by flaming the yellow solid residue.

b. Dehydrohalogenation Method

Into one arm of a Pyrex H-tube, the two arms of which were joined through a sintered disc, was condensed 1.6716 g. (16.52 mmoles) of triethylamine, 62.1 cc. (2.77 mmoles) of ammonia, 123.5 cc. (5.51 mmoles) of methylamine, 1.5545 g. (8.37 mmoles) of methyldibromoborine and 30 ml. of anhydrous benzene. After standing at room temperature for three days the reaction mixture was filtered through the sintered disc to remove by-product ammonium salts. These salts were washed three times by condensing the solvent back into the reaction arm. An aqueous solution of the by-product ammonium salts contained 13.49 mmoles N, 14.39 mmoles Br and 0.66 mmole B. The filtrate arm was sealed from the H-tube and opened to the vacuum line. The filtrate was fractionally condensed through a -15°C. trap which retained a small quantity of colorless liquid. An aqueous solution of the nonvolatile orange solid residue contained 1.76 mmoles B, 1.42 mmoles N and 1.09 mmoles Br. No additional material was isolated by passage of the benzene solvent through a -22.8°C. trap. The benzene was extracted with one 10 ml. and two 5 ml. portions of water. The aqueous extract contained 0.36 mmole B, 0.40 mmole N and < 0.025 mmole Br. The crude borazene fraction retained by the -15°C. trap was fractionally condensed through traps at 5°C. and -5°C. A 0.039 g. (10%) fraction of colorless liquid passing both traps was identified as crude N-methyl-B-trimethylborazene. Observed vapor tension 3.5 mm./25°C. (Lit.²⁹, 3.3 mm./25.0°C.).

The infrared spectrum contained a band at 2.92 μ (w) due to N-H stretching and one in the 6.8 μ (vs) region due to B-N ring oscillation. The remaining liquid which was retained at 5°C. was passed through a 10°C. trap and yielded 0.0677 g. (16%) of crude N-dimethyl-B-trimethylborazene. The infrared spectrum was identical with that of a sample obtained by the pyrolysis method except for minor bands at 6.25 μ , 8.05 μ , 10.17 μ and 13.64 μ .

2. Methylamine Trimethylborine
and Ammonia Trimethylborine

Into a 12-l., 7-neck round-bottom flask fitted with a Hershberg stirrer, a cold finger condenser and 2-l. addition funnel was placed 576.5 g. (23.70 moles) of magnesium turnings and 7500 ml. of di-n-butyl ether. To this stirred mixture was added 2268 g. (23.89 moles) of methyl bromide over a period of 4-5 hrs. after initiating the reaction with a small quantity of previously prepared Grignard. The temperature of the reaction mixture was held in the range 20-40°C. with an ice-bath during the methyl bromide addition. A solution of 521 g. (7.67 moles) of boron trifluoride in 1154 g. (8.87 moles) di-n-butyl ether was added dropwise over a 3-4 hr. period, using an ice-bath to maintain a temperature of 25-40°C. Very little evolution of trimethylborine was observed until the reaction mixture was heated. Following the addition of the boron trifluoride butyl etherate, the reaction mixture was heated slowly, with stirring, to 80°C. over a period of 7 hrs., during which time the product trimethylborine was smoothly evolved and absorbed in 300 g. (9.67 moles) anhydrous methylamine in a 3-l., 4-neck flask fitted with two adjustable gas inlet tubes, an amine addition tube, and a Dry Ice condenser.

A second preparation following the same procedure was made using the following quantities of reagents: 596.5 g. (24.53 moles) magnesium, 7500 ml. di-n-butyl ether, 2268 g. (23.89 moles) methyl bromide, and 507 g. (7.47 moles) boron trifluoride in 1224 g. (9.40 moles) di-n-butyl ether. The portion of the trimethylborine evolved on heating the reaction mixture between 20°C. and 42°C. was completely absorbed in the excess methylamine remaining after formation of methylamine trimethylborine produced in the first preparation, and that portion evolved between 42°C. and 80°C. was completely absorbed in 144 g. (8.45 moles) anhydrous ammonia in a similar manner. The excess of methylamine and ammonia was removed by vacuum distillation through a Dry Ice condenser leaving each of the addition compounds as a colorless solid. The yields of methylamine trimethylborine and ammonia trimethylborine were 474 g. (5.45 moles) and 316 g. (4.33 moles), respectively, representing an over-all 64.6% yield of trimethylborine.

3. N-Trimethyl-B-dimethylborazene

Into a nitrogen-swept 1-l. flask equipped with Hershberg stirrer, water reflux condenser and a 250 ml. dropping funnel were placed 5.50 g. (44.9 mmoles) of N-trimethylborazene and 130 ml. of anhydrous diethyl ether. The flask was immersed in a 20°C. water bath and 30.0 ml. of 2.94M (88.2 mmoles) ethereal methylmagnesium bromide diluted with 160 ml. of anhydrous diethyl ether was added dropwise to the vigorously stirred solution during 2 hrs. The resulting reaction mixture was stirred for 1.5 hrs. at room temperature and then decomposed with 10 ml. degassed saturated ammonium chloride. The colorless ether layer was pressure siphoned into a flask containing anhydrous sodium sulfate. Analysis of an aqueous solution of the precipitated magnesium salts indicated 8.3 mmoles B (6.2%). After 1.5 hrs. the ether solution, which had become turbid, was filtered through sintered glass and the filter cake washed with three 5 ml. portions of ether. Analysis of a methanol extract of the filter cake indicated 26.8 mmoles B (19.9%). The combined filtrate and ether washings were stripped of solvent by distillation. Residual volatile materials were transferred to the vacuum line and separated into the following components by fractional condensation:

- (I) Residual ether: passed -63.5°C. cold trap.
- (II) N-Trimethylborazene; 0.054 g. (0.440 mmole, 1.0%) passed -22.8°C. trap, stopped -45.2°C. trap, v.t. 12.2 mm./26.2°C.; reported for $H_3B_3N_3(CH_3)_3$: 11.9 mm./25.0°C.²⁹
- (III) Crude N-trimethyl-B-methylborazene; 0.062 g. (0.454 mmole, 1.0%) passed -10°C. trap, stopped by -22.8°C. trap, v.t. 3 mm/25°C.
- (IV) N-Trimethyl-B-dimethylborazene; low melting solid (ca. 40°C.), 0.535 g. (2.99 mmoles, 8.3%), passed 10°C. trap, stopped by 0°C. trap, v.t. 1 mm./25°C. The infrared spectrum had a B-H stretching band at 4.05 μ (m) and a band due to B-N ring oscillation at 6.8 μ (vs).
- (V) Crude hexamethylborazene; 0.147 g. (0.893 mmole, 2.0%), stopped by 10°C. trap. The principal contaminant was a low melting solid, presumably the pentamethyl compound.

The nonvolatile residue was extracted with ether. Analysis of an aqueous solution of the ether insoluble residue indicated the presence of only

1.27 mmoles B (1%). The ether extract was evaporated to dryness and the resulting 3.41 g. colorless solid residue recrystallized from acetonitrile. A 0.769 g. (4.67 mmoles, 10.6%) quantity of crude hexamethylborazene was obtained in two crops. The infrared spectra of both crops contained a band at 4.05μ (w) due to B-H stretching, suggesting that the principal contaminant was N-trimethylborazene-B-dimethyl. Evaporation of the acetonitrile mother liquor yielded 1.43 g. of an unidentified colorless solid which showed no B-H on infrared analysis. Absence of the B-N ring oscillation band near 6.8μ in its infrared spectrum indicated that the solid was not a borazene derivative.

A second experiment with a few exceptions in procedure noted below was done using the following quantities of reagents: 100 ml. of 3M methylmagnesium iodide (0.3 mole) in 150 ml. diethyl ether was added to 17.6 g. (0.144 mole) of N-trimethylborazene in 700 ml. ether. The mixture was refluxed 2.5 hrs., cooled to 10°C ., and hydrolyzed with 140 ml. saturated ammonium chloride solution. The organic phase was immediately filtered through anhydrous sodium sulfate and dried over an additional quantity of the same desiccant. Fractional distillation of the ethereal solution yielded no borazene derivatives and left an unidentified solid residue.

4. Methylaminoborine Trimer

Into a 12-l., 7-neck round-bottom flask fitted with a Hershberg stirrer, cold finger condenser and 2-l. addition funnel was placed 451.5 g. (11.90 moles) of powdered lithium aluminum hydride and 3800 ml. anhydrous diethyl ether. The addition funnel contained a boron trifluoride etherate solution freshly prepared by dissolving 1192 g. (17.58 moles) of boron trifluoride in 1228 g. (16.60 moles) of anhydrous ether at -78°C . The boron trifluoride etherate was added to the ethereal lithium aluminum hydride over approximately 4 hrs. with stirring while the flask was immersed in an ice-bath. The diborane generated was absorbed in 330 g. (10.63 moles) of methylamine in a 3-l., 4-neck flask fitted with an adjustable gas inlet tube, amine addition tube, and Dry Ice condenser.

A second run was made in which 1078 g. (15.90 moles) boron trifluoride in 1198 g. (16.18 moles) anhydrous ether was added during 3 hrs. to 455.8 g. (12.01 moles) lithium aluminum hydride in 3800 ml. anhydrous ether. The resultant diborane was reacted with an additional 355 g. (10.79 moles) anhydrous methylamine, which had been condensed onto the product from the first run. The methylamine borine weighed 936 g. (20.8 moles, 97.4% based on methylamine). This adduct was placed in a 4-l. resin flask and heated slowly to 100°C . at which temperature an extremely vigorous exothermic evolution of hydrogen occurred resulting in considerable loss of methylaminoborine trimer; yield, 702 g. (78.5%).

A small portion of the trimer was purified by high vacuum sublimation to obtain an infrared spectrum (KBr disc). No melting point was observed up to 200°C . where decomposition into liquid N-trimethylborazene occurs. Another small sample was recrystallized from absolute methanol without decomposition, in agreement with Bissot and Parry.³⁰

5. Attempt to Prepare Decamethylbaborazyl

Into a 40 ml. glass bomb tube were condensed 0.3788 g. (2.514 mmoles) of N-trimethyl-B-dimethylborazene and 0.3747 g. (2.487 mmoles) of N-dimethyl-B-trimethylborazene. The sealed tube was heated at a series of temperatures. After

each pyrolysis the tube was opened and noncondensable gases removed. The results of these pyrolyses are tabulated in Table V.

The pyrolysis residue was separated into the following fractions by a combination of fractional sublimation and fractional condensation:

- (I) 0.0263 g. volatile liquid, v.t. ~ 3 mm./ 25°C .; presumably N-trimethyl-B-methylborazene and/or N-methyl-B-trimethylborazene.
- (II) 0.0847 g. slightly volatile high melting liquid, v.t. ~ 1 mm./ 25°C .; identified by infrared as a mixture of N-trimethyl-B-dimethylborazene and N-dimethyl-B-trimethylborazene.
- (III) 0.2243 g. moist colorless solid; identified by infrared as impure hexamethylborazene.
- (IV) 0.0714 g. of sublimate collected between 80 - 140°C . / < 1 mm. ranging from colorless crystalline solid to colorless viscous liquid. The infrared spectrum of the more volatile crystalline solid contained the typical band at 6.9μ (vs) due to B-N ring oscillation and a band due to B-H stretching at 4.05μ .

The sublimation residue consisted of 0.2399 g. of a clear colorless glass, the infrared spectrum of which contained bands at 2.91μ (w) and 4.04μ (w) due to N-H and B-H stretching. The B-N ring oscillation was observed in the 6.8μ (vs) region. Found upon elemental analysis: C, 31.36-28.94; H, 7.54-7.37; B, 22.4; N, 30.70. The molecular weight was determined isopiesticly in benzene as 438.

6. Pyrolysis of N-Trimethyl-B-dimethylborazene

A 0.1263 g. (0.8383 mmole) quantity of N-trimethyl-B-dimethylborazene was condensed into a 5 ml. glass bomb tube. The sealed tube was maintained at 375°C . for 15 hrs., opened and 1.42 cc. of hydrogen removed. No additional noncondensable gas was evolved upon heating the tube at 385°C . for 16 hrs. and at 395°C . for 20 hrs.

7. Pentamethyl-B-chloroborazene

Employing the method previously described,¹⁷ 5.25 g. (23.2 mmoles) of N-trimethyl-B-trichloroborazene was treated with 46.4 mmoles of ethereal methyl-lithium. Filtration of the resultant reaction mixture removed suspended solids which contained 47.6 mmoles Li^+ , 48.4 mmoles Cl^- , 0.55 mmole I^- and 0.65 mmole N. Solvent was removed from the filtrate on the Rinco evaporator. The brownish solid residue was extracted with one 100 ml. and two 50 ml. portions of petroleum ether (b.r. 20 - 40°C .). The petroleum ether-insoluble solids were further extracted with three 40 ml. portions of benzene. The residue obtained by evaporation of the orange benzene extract could not be vacuum sublimed. An aqueous solution of this material contained 28.0 mmoles Li^+ , 0.36 mmole Cl^- , 28.35 mmoles I^- , 1.70 mmoles B and 0.61 mmole N. An aqueous solution of the benzene-insoluble solid contained 14.8 mmoles Li^+ , 0.92 mmole Cl^- , 14.63 mmoles I^- , 0.57 mmole B and 0.68 mmole N. The light yellow petroleum ether extract was stripped of solvent on the Rinco evaporator, leaving a yellow solid residue. That portion of the residue which was volatile below 130°C . was removed by vacuum sublimation. The nonvolatile residue was slowly decomposed by water and contained 2.8 mmoles Li^+ , 2.82 mmoles

TABLE V
Pyrolysis of Equimolar Mixture
of Isomeric Pentamethylborazenes

T, °C.	Time, hrs.	Total Gas Volume, cc.
100	15	1.52
150	15	4.70
200	15	5.25
250	15	5.54
250 ^(a)	15	6.40
260-310	27	7.27
345-355	17	11.43 ^(b)
380	17	36.80
380-390	15	81.2 ^(c)

- (a) Reactants transferred from a 40 ml. to a 5 ml. glass bomb tube.
- (b) Appreciable methane observed in noncondensable gas.
- (c) Consisted of 63.6 cc. methane and 17.5 cc. hydrogen; determined by combustion over cupric oxide.

Cl^- , 1.64 mmoles I^- , 9.64 mmoles N and 9.28 mmoles B. The nearly colorless sublimate was resublimed at 50°C . under high vacuum to yield 2.73 g. (63%) of colorless pentamethyl-B-chloroborazene; melting range $120-28^\circ\text{C}$. Anal. calcd. for $\text{C}_5\text{H}_{15}\text{B}_3\text{N}_3\text{Cl}$: Cl, 19.15. Found: Cl, 18.98.

In a second, but unsuccessful experiment, 200 ml. of an ethereal methyl-lithium solution containing 195 mmoles of methyllithium and 28.2 mmoles of lithium ethoxide was added dropwise during 4 hrs. to a stirred solution of 22.0 g. (97.5 mmoles) of N-trimethyl-B-trichloroborazene in 950 ml. diethyl ether, maintained at $2 \pm 2^\circ\text{C}$. and contained in a nitrogen-swept 2-l. round-bottom flask fitted with a Hershberg stirrer, 250 ml. dropping funnel and a metal thermometer. The stirred solution was warmed to room temperature during 1 hr. and stored overnight. Filtration removed by-product lithium chloride. Analysis of an aqueous solution of these salts indicated 222 mmoles Cl^- , 224 mmoles of Li^+ and 0.71 mmoles of I^- . A 500 ml. quantity of benzene was added to the filtrate and the ether removed by distillation. The inorganic salts thereby precipitated were collected by filtration. Analysis of an aqueous solution of these salts indicated 73.4 mmoles Cl^- , 102 mmoles I^- , 182 mmoles Li^+ and 0.68 mmoles B. Benzene was removed from the filtrate in a Rinco evaporator, leaving a tacky sludge which was then fractionally condensed in traps maintained at room temperature and -10°C . At temperatures up to 90°C . a 1.3 g. mixture of orange liquid and colorless solid was evolved and collected at -10°C . The remaining highly viscous residue was brush flamed to remove a quantity of yellow-orange fluid liquid leaving a nonvolatile, nearly colorless residue. This residue was extracted with hot benzene. Upon concentrating the benzene solution, gelation occurred. Removal of the solvent yielded 2.24 g. of a light brown noncrystalline solid, the infrared spectrum of which showed bands near 7.3μ and 12.5μ which are similar to those found in the spectrum of boron nitride. Analysis of an aqueous solution of the benzene insoluble portion of the sublimation residue indicated 2.45 mmoles Cl^- , 64 mmoles I^- , 67.1 mmoles Li^+ , and 17.4 mmoles boron. The receiver which contained the yellow-orange distillate was sealed to a series of four receivers and heated under high vacuum.

Following the removal of 0.25 g. of forerun, 9.28 g. of slightly yellow liquid distillate containing minor quantities of colorless solid was obtained at 55°C . Infrared analysis showed a typical B-N band due to the borazene ring near 7μ . Analysis of a hydrolyzed sample indicated: B, 18.0; N, 19.8; Cl, 0.91. A 0.455 g. quantity of distillate possessing similar physical characteristics was obtained between 55°C . and 95°C . The viscous brown liquid residue weighed 0.92 g.

8. Attempt to Prepare N-Dimethyl-B-trichloroborazene

A mixture presumably containing ammonia trichloroborine and methylamine trichloroborine which had been prepared from 453.2 cc. (20.23 mmoles) of methylamine, 225.1 cc. (10.05 mmoles) of ammonia and 678.4 cc. (30.29 mmoles) of boron trichloride was slurried with 125 ml. of dry toluene in a 500 ml. 3-neck round bottom flask. During 30 min. a solution of 6.068 g. (59.97 mmoles) of triethylamine in 100 ml. of toluene was added to the stirred suspension at 0°C . After stirring the reaction mixture for an additional 30 min. at 0°C . and 4 hrs. at room temperature, suspended solids were removed by filtration through sintered glass. An aqueous solution of the filter cake contained 55.90 mmoles Cl^- , 53.46 mmoles N and 12.01 mmoles B. Solvent was stripped from the filtrate on the Rinco evaporator and the residue heated to 180°C . under high vacuum. The sublimate thereby obtained was fractionally sublimed under high vacuum. Between $70-120^\circ\text{C}$.

0.2659 g. of impure sublimate ranging from light brown solids to light brown viscous liquids were obtained. No attempt was made to further fractionate the residual 0.4640 g. of brownish-orange viscous liquid. The brown solid residue which was not sublimable at 180°C. weighed 1.129 g. and was only partially soluble in benzene, 0.303 g. being extracted by such treatment.

9. 8-Bora-7,9-diazaro-peri-naphthene

A solution of 2.0 g. (17 mmoles) of boron trichloride in 25 ml. of benzene was added dropwise at room temperature in about 25 min. to 2.8 g. (17.7 mmoles) of 1,8-diaminonaphthalene (recrystallized three times from 95% ethanol) dissolved in 65 ml. of benzene contained in a 200 ml., 3-neck round-bottom flask fitted with a nitrogen inlet, magnetic stirrer, self equalizing dropping funnel and condenser. The flask was swept with dry nitrogen prior to the addition of the reactants. The condenser exit gases were passed successively through a -78°C. trap and a sodium hydroxide scrubber. After about one-fourth of the boron trichloride had been added, the purple solution turned yellow-brown, became thick and rendered the stirrer ineffective. Another 50 ml. of benzene was added and agitation was resumed by mechanically shaking the whole apparatus. The mixture warmed slightly during addition of the boron trichloride and was an olive-drab color after addition had been completed. The mixture was refluxed overnight and then swept with nitrogen. Boron and chlorine analyses of the scrubber contents indicated 64.2% of the expected hydrogen chloride had been evolved.

About two-thirds of the solvent was removed under water aspirator pressure and then 25 ml. of ether was added followed by the dropwise room temperature addition during 1 hr. of 80 ml. of a 0.39M (31 mmoles) solution of lithium aluminum hydride in ether. The solution was refluxed 1 hr. and then allowed to remain at room temperature overnight. The excess hydride was hydrolyzed by slow addition of 21 ml. of 6N hydrochloric acid. The ether solution was immediately decanted from the aqueous acid layer and combined with three 20 ml. ether washes of the aqueous layer. The yellow ether solutions were dried over anhydrous magnesium sulfate, treated with decolorizing carbon, filtered, evaporated on a steam bath and in a stream of nitrogen at room temperature, and finally dried in vacuum. The crude yellow-brown product weighed 1.804 g. (60.7%) and turned purple on standing in air. The crude product was purified by sublimation in high vacuum to give 1.252 g. (42.1%) of purified material. Further purification was attempted by crystallization but methanol was inadvertently used and reacted with the product. The product was immediately precipitated from the methanol by addition of water, dried and resublimed to give an almost colorless solid which was recrystallized three times from *n*-hexane and sublimed twice to give a very pale pink sublimate, m.p. 97-99°C. (under nitrogen). (Anal. calcd. for $C_{10}H_9N_2B$: C, 71.48; H, 5.40. Found: C, 71.34; H, 5.34). The infrared spectrum (KBr disc) showed N-H and B-H absorption and the ultraviolet spectrum had $\lambda_{max} 238 m\mu$ ($\log \epsilon$, 4.60).

10. Methoxy-8-bora-7,9-diazaro-peri-naphthene

Crude 8-bora-7,9-diazaro-peri-naphthene obtained from *n*-hexane mother liquors (vide supra) was partially purified material having m.p. 86-93°C. and 0.1495 g. (0.8898 mmole) was sealed in an 8 ml. heavy-wall bomb tube with about 1.5 ml. of methanol (dried with Mg and distilled). The tube was allowed to remain at room temperature for 2 days then heated for 1 hr. at 100°C. The tube was opened but the hydrogen was inadvertently lost. The contents of the tube recrystallized

from dry methanol as colorless needles which were sublimed at 60-100°C. in high vacuum to give 0.0600 g. (34.1%) of colorless product, m.p. 115-20°C. (uncorr.). (Anal. calcd. for $C_{11}H_{11}ON_2B$: C, 66.70; H, 5.60. Found: C, 66.55; H, 5.68). The infrared spectrum (KBr disc) showed N-H but no B-H bands. The ultraviolet spectrum had $\lambda_{\max}^{232 m\mu}$ (log ϵ , 4.84). The crude residue from the mother liquor amounted to 0.0997 g. (56.6%).

11. Pyrolysis of 8-Bora-7,9-diazaro-peri-naphthene with Dimethylphosphine

Into a 10 ml. heavy-wall bomb tube containing 0.1762 g. (1.049 mmoles) of 8-bora-7,9-diazaro-peri-naphthene was condensed 48.23 cc. (2.152 mmoles) of dimethylphosphine. The tube was sealed and remained at room temperature overnight, then was heated to 60°C. for about 5 min. whereupon the yellow solid dissolved but crystallized out upon cooling to room temperature. The tube was opened and 48.25 cc. (2.153 mmoles) of dimethylphosphine were recovered. A portion of the yellow residue, m.p. 96-99°C. (uncorr.), weighing 0.1410 g. (0.8392 mmole) was transferred to another bomb tube together with all of the dimethylphosphine. The tube was sealed and heated at $180 \pm 10^\circ\text{C}$. for 16 hrs. The tube was opened and 4.77 cc. (0.213 mmole) of hydrogen were obtained. The tube was resealed and heated at $200 \pm 10^\circ\text{C}$. for 18 hrs. and 11.87 cc. (0.529 mmole) of hydrogen were obtained. The tube was again sealed and heated at $210 \pm 5^\circ\text{C}$. for 7 hrs. but the hydrogen was accidentally lost. The total hydrogen measured was 88% of theoretical. The dimethylphosphine was collected and identified by vapor tension. It amounted to 44.8 cc. (2.00 mmoles) or 92.9% recovery.

The yellow residue was removed mechanically with the aid of benzene which was removed under vacuum. The residue, 0.1227 g. (87.6%) sintered at 222°C., appeared to melt partially at 275°, 295° and 351°C., and finally melted to a red liquid at about 410°C. The infrared spectrum (KBr disc) showed N-H to be present but B-H was almost nonexistent. The product was insoluble in common organic solvents but the yellow coloration was removed by washing with methanol. The resulting colorless powder, 0.0708 g. (50.6%) did not melt below 410°C. under nitrogen and turned only slightly tan during the heating period. (Anal. calcd. for $C_{10}H_7BN_2$; C, 72.35; H, 4.25. Found: C, 72.02; H, 5.01). The infrared spectrum (KBr disc) showed N-H but no B-H bands.

F. Thiosiloxanes

1. Reaction of Diorganodichlorosilanes with Hydrogen Sulfide

Each of the experiments summarized in Table IV were done in a generally similar manner so that only two experiments are described.

a. Dimethyldichlorosilane

In Experiment 3 anhydrous hydrogen sulfide was bubbled for 0.5 hr. at room temperature into a solution of 39.5 g. (0.5 mole) of pyridine (dried over CaH_2) in 250 ml. of benzene (dried over Na) contained in a 1-l. 3-neck flask fitted with stirrer, gas introduction tube and reflux condenser protected by a calcium chloride tube. A dropping funnel was then substituted for the gas introduction tube and 32.25 g. (0.25 mole) of dimethyldichlorosilane was added dropwise over a period of 1 hr. The temperature rose to a maximum of 49°C. and pyridine hydrochloride

slowly precipitated. Hydrogen sulfide introduction was resumed at a slow rate for an additional hour. The pyridine hydrochloride (41 g.) was separated by filtration in a dry nitrogen atmosphere and the clear filtrate distilled until the pot temperature reached 100°C. Additional material, volatile at 70°C. under aspirator vacuum, was removed leaving a light yellow liquid residue weighing 15.1 g. D.T.A. cryoscopic molecular weight determination of this material in benzene gave a value of 187 ± 5 . The residue appeared to decompose with gas evolution above 100°C., distilled at 175-200°C. and immediately solidified in the air condenser. The light yellow solid (12.1 g.) was dissolved in 30 ml. of boiling hexane, filtered and allowed to crystallize to long needles, m.p. 109-12°C.; M.W. (by D.T.A. cryoscopic in benzene) 218 ± 10 , calcd. $[(CH_3)_2SiS]_2$, 180.45.

b. Diphenyldichlorosilane

In Experiment 5 anhydrous hydrogen sulfide was bubbled rapidly for 10 min. at room temperature into a solution of 39.5 g. (0.5 mole) of pyridine (dried over CaH_2) in 250 ml. of benzene (dried over Na) contained in a 1-l. 3-neck flask fitted with stirrer, gas introduction tube and reflux condenser protected by a calcium chloride tube. A dropping funnel was then substituted for the gas introduction tube and 63.25 g. (0.25 mole) of diphenyldichlorosilane was added dropwise with stirring over a period of 15 min. The temperature rose to 42°C. during this time and pyridine hydrochloride slowly precipitated. When addition was complete, H_2S was introduced for an additional 30 min. after which the mixture was warmed to 60-70°C. for an hour while stirring was maintained. The pyridine hydrochloride (about 40 g.) was separated by filtration in a dry nitrogen atmosphere and the clear filtrate was distilled until the pot temperature reached 115°C. A light yellow oil remained from which white crystals separated at room temperature. The crystals (38.6 g.) were filtered and washed with toluene. Recrystallization of this material from benzene-hexane gave white crystals with a wide melting range of 140-85°C. Molecular weight determinations (D.T.A. cryoscopic in benzene) gave a value of 840 ± 25 . A 10.0 g. quantity of this material was heated in an atmosphere of nitrogen to 240°C. for 15 min. No gas evolution was apparent. The residual glass slowly crystallized on cooling. The material was dissolved in a hot benzene-hexane mixture and crystallized at room temperature to fine crystals (wt. 6.95 g.; m.p. 130-36°C.). A D.T.A. cryoscopic molecular weight determination of this material in benzene indicated a value of above 800. An isopiestic molecular weight determination in benzene at 41.9°C. using azobenzene as standard has not yet equilibrated but the maximum value is indicated to be 600; calcd. for $[(C_6H_5)_2SiS]_3$, 643.11.

2. Attempts to Detect Sulfhydryl Groups in Thiosiloxane Products

a. Reaction Product from Diphenyldichlorosilane

A total of 8.90 g. of solid product from Experiment 6 (Table IV) was dissolved in 30 ml. of benzene (dried over Na). After a trace of insoluble material was separated by filtration, 1.6 g. (20 mmoles) of pyridine (dried over CaH_2) was added to the solution. No visible precipitate formed in 1 hr. and 2.60 g. (11 mmoles) of redistilled diphenyldichlorosilane was added with immediate formation of a trace of fine white precipitate. No further precipitation occurred on standing 6 days at room temperature in a well stoppered flask. The solution was then saturated with dry hydrogen sulfide. On standing overnight separation of long needles of pyridine hydrochloride (2.21 g., 19 mmoles) was observed. The decantate was evaporated on a steam bath in a stream of nitrogen leaving a solid residue (m.p. 110-80°C.).

b. Reaction Product from
Dimethyldichlorosilane

A total of 2.43 g. of liquid product from Experiment 4 (Table IV) was dissolved in 10 ml. of benzene (dried over Na) with care being taken to exclude moisture. To this was added 1.96 g. (25 mmoles) of pyridine (dried over CaH_2) and 1.14 g. (12.5 mmoles) of redistilled dimethyldichlorosilane in 7 ml. of dry benzene. Only a faint trace of white precipitate appeared which did not increase in amount during three days. All material volatile at 60°C./15 mm. was then removed with an aspirator separated from the system by a calcium chloride tube. To the residue was added 0.5 g. (6 mmoles) of dry pyridine and 10 ml. of dry benzene followed by saturation of the solution with H_2S . Only a faint trace of white solid had separated after one day. All material volatile at 60°C./15 mm. was again removed, the fluid yellow residue heated to 200°C. and the resulting white needles recrystallized from hexane (m.p. $108\text{--}12^\circ\text{C.}$).

3. Reaction of Diorganodichlorosilanes
with Hydrogen Sulfide in the Presence
of Trimethylchlorosilane

The preparations summarized as Experiments 7 and 8 in Table IV were done in a generally similar manner so that only Experiment 7 is described.

a. Diphenyldichlorosilane

Anhydrous hydrogen sulfide was bubbled for 1 hr. at room temperature into a solution of 63.25 g. (0.25 mole) of redistilled diphenyldichlorosilane, 8.70 g. (0.08 mole) of redistilled trimethylchlorosilane and 45.8 g. (0.58 mole) of pyridine (dried over CaH_2) in 250 ml. of benzene (dried over Na) contained in a 1000 ml. 3-neck flask fitted with a gas introduction tube, stirrer and reflux condenser protected by a calcium chloride tube. The temperature rose to a maximum of 55°C. and pyridine hydrochloride slowly precipitated. After hydrogen sulfide introduction was terminated, the contents of the flask were allowed to stand for 1 hr. without stirring followed by filtration in a dry nitrogen atmosphere to separate 56.5 g. (0.49 mole) pyridine hydrochloride.

Addition of 0.5 g. of trimethylchlorosilane and 0.5 g. of pyridine to the filtrate produced no more precipitate on standing overnight. The clear filtrate was distilled to a pot temperature of 90°C. and the residue was stripped of additional volatile material at 60°C. using an aspirator and Rinco evaporator.

The viscous residue crystallized on cooling and then was twice recrystallized from benzene to give well formed crystals (40.2 g., m.p. $192\text{--}94^\circ\text{C.}$). A D.T.A. cryoscopic molecular weight determination of this material in benzene indicated a value of 594. An isopiestic molecular weight determination in benzene at 93.4°C. using azobenzene as a standard indicated a maximum value of 448. Infra-red spectra showed no aliphatic C-H or $\text{CH}_3\text{-Si}$ bonds. Found: C, 67.35; H, 4.62; Si, 12.9; S, 14.4. Calcd. for $[(\text{C}_6\text{H}_5)_2\text{SiS}]_3$: C, 67.29; H, 4.67; Si, 13.08; S, 14.95; MW, 643.13.

The combined filtrate from the recrystallization of the solid product was concentrated on a steam bath in a stream of nitrogen leaving a tan viscous liquid residue (9.8 g.) which did not crystallize. The viscous oil was distilled at reduced pressure (5 mm.) through a 4 in. vacuum-jacketed Vigreux column to yield the following fractions:

I	110-13°C.	0.20 g.
II	113-22°C.	0.36 g.
III	122-202°C.	0.34 g.
IV	202-50°C. (mostly 240-50°C.)	1.50 g.
V	250-60°C.	1.90 g.

The still pot residue weighed 2.43 g. and was a brown, very viscous solid. D.T.A. cryoscopic molecular weight determinations in benzene on Fraction V and on the pot residue gave values of 720 and 713, respectively. No evidence of the presence of methyl groups was found in these substances using infrared spectroscopy.

A total of 8.86 g. of solid material (presumably $[(C_6H_5)_2Si]_3$, m.p. 192-94°C.) from Experiment 7 (vide supra) was heated in a 100 ml. round bottom flask fitted with a 6 in. length of 40 mm. glass tubing into which a slow stream of dry nitrogen was introduced. The temperature was maintained at 245-60°C. with a heating mantle for 3 hrs. without evidence of gas evolution but a small amount of white solid was observed to sublime on the cooler walls. The melt on cooling began to crystallize but was dissolved in 50 ml. of hot benzene and transferred to a reduced pressure distillation apparatus with a 4 in. vacuum-jacketed Vigreux column. After the benzene was removed only a trace of material distilled at 290-300°C./4 mm. at a pot temperature of about 350°C. The distillate and material which condensed on the walls of the distilling flask and columns were dissolved in benzene which on evaporation left a sticky residue (0.4 g., m.p. 110-40°C.).

The major portion of the material in the still pot set to a clear glass (8.1 g.) which was soluble in, but did not crystallize from benzene. Molecular weight determinations by the D.T.A. cryoscopic method showed a value of 832 and by the isopiestic method in benzene with azobenzene as standard gave a maximum value of 644.

b. Dimethyldichlorosilane

In Experiment 9 (Table IV) a total of 1.85 g. (0.054 mole) of anhydrous hydrogen sulfide was bubbled into a 100 ml. test tube-shaped container fitted with a gas introduction tube and exit tube protected by a calcium chloride tube and containing 25 ml. of benzene (dried over Na), 5.5 g. (0.05 mole) redistilled trimethylchlorosilane and 4.0 g. (0.05 mole) pyridine (dried over CaH_2). White crystals (2.7 g.) of pyridine hydrochloride precipitated during 1 hr. at room temperature and were separated by filtration.

The filtrate was added dropwise to a nitrogen-filled 1000 ml. 3-neck flask fitted with gas introduction tube, mechanical stirrer and interchangeable dropping funnel and reflux condenser protected by a calcium chloride tube and containing 32.25 g. (0.25 mole) of redistilled dimethyldichlorosilane and 43.5 g. (0.55 mole) of dry pyridine in 200 ml. of dry benzene. Pyridine hydrochloride separated on introduction of the filtrate. Anhydrous hydrogen sulfide was bubbled into the flask for 1 hr. with stirring. The temperature rose to a maximum of 45°C. and pyridine hydrochloride slowly separated. After termination of hydrogen sulfide introduction, 5.5 g. (0.05 mole) of trimethylchlorosilane

was added and the mixture was allowed to stand overnight. Hydrogen sulfide was introduced for an additional 0.5 hr. and the excess was swept out by bubbling in dry nitrogen. The voluminous precipitate of pyridine hydrochloride (36.5 g.) was separated by filtration in a nitrogen atmosphere. The filtrate was stripped of volatile material by distillation on a steam bath followed by rotation on a Rinco evaporator at 60°C./15 mm.

The yellow liquid residue (15.12 g.) did not crystallize on cooling. Addition of 3 g. (0.028 mole) trimethylchlorosilane and 3 g. (0.038 mole) of anhydrous pyridine produced only a trace of precipitate after ten days standing. The solution was filtered and evaporated on a Rinco apparatus at 60°C./15 mm.

The fluid tan filtrate was heated with mild effervescence to 200°C. for 2 hrs. in an atmosphere of nitrogen and on cooling it partly crystallized. The material was too soluble in hexane, benzene, carbon tetrachloride, chloroform, ethyl acetate or various mixtures thereof for successful recrystallization. The material was then distilled at atmospheric pressure on a short path distillation apparatus yielding 10.9 g. of yellow oily distillate which partially crystallized on cooling and 0.5 g. of black tarry residue in the still pot. The white solid material, which had a tendency to sublime, distilled in large part at 170-80°C. and the yellow oil came over at 180-205°C. Recrystallization of the distillate from hexane gave 3.22 g. of white needles (m.p. 112-13°C.). Evaporation of the filtrate left 4.0 g. of a yellow fluid liquid.

IV. SUMMARY AND CONCLUSIONS

Additional study of the variables affecting the yield and degree of polymerization of linear phosphinoborine polymers revealed that when the base strength of the amine end-group significantly exceeds that of the secondary phosphine the latter cannot successfully compete for the acid borine and polymer yield drops rapidly. The predicted formation of linear polymers from a mixture of secondary phosphine and triethylamine borane was demonstrated.

Dimethylphosphinoborine polymer was chlorinated using aluminum chloride-catalyzed carbon tetrachloride in conventional equipment. Methyl ethylphosphinoborine polymer could not be completely chlorinated (55%) using aluminum chloride-catalyzed methyl chloride. Dimethylphosphinodichloroborine polymer on pyrolysis failed to yield the corresponding trimer in contrast to the unsubstituted polymers. Similarly, dimethylphosphinodichloroborine trimer was not formed by dehydrohalogenation of dimethylphosphine trichloroborine or by pyrolysis of trimethylphosphine trichloroborine suggesting that B-chloro substituents prevent cyclization of phosphinoborines.

A series of attempts to prepare B-cyano-derivatives of dimethylphosphinoborine trimer were unsuccessful. The quantitative nature of the preparative reaction of dimethylphosphinodifluoroborine trimer was established.

Tri- and tetraatomic cyclic secondary phosphines have been prepared and shown to be unstable at ambient temperatures. Methylallylphosphine borine is unstable with respect to addition of the borine moiety to the olefinic unsaturation.

Preparation of the two isomeric pentamethylborazenes has been accomplished but copyrolysis of these materials produced both hydrogen and methane as well as polymeric borazene derivatives. The polymerization of borazene nuclei has been demonstrated again but not in a manner permitting definitive structural assignments to the polymer. The pseudoaromatic B-N compound, 8-bora-7,9-diazaroperi-naphthene, has been prepared and studied briefly.

An initial investigation of thiosiloxane polymers was undertaken with the preparation of the dimethyl- and diphenyl-derivatives.

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APPENDIX I

Some Physical and Chemical Properties of Phosphinoboranes

Monomer Unit	D.P.	m.p., °C.	b.p., °C.	Form at 20°C.	S.I.T., °C.	% Hydrolysis 24 hrs. at 202°C.	Ref.
H ₂ PBH ₂	high	dec.	-	waxy solid	-	-	31
F ₂ PBF ₂	1	-	-	liquid (-80°)	-	100	32
H ₂ PB(CH ₃) ₂	28	-	dec.	oil	25	-	33
H ₂ PB(C ₄ H ₉) ₂	~2	-	-	liquid	-	-	34
CH ₃ HPBH ₂	-	-	dec.	oil	-	-	33
CH ₃ HPB(CH ₃) ₂	-	-	-	oil	-	-	11
(CH ₃) ₂ PBH ₂	3	86-7	235	cryst. solid	244	0.08	11,33
	4	160-1	310	cryst. solid	233	0.0	11,33
	~10	-	dec.	solid	-	-	35
	43	163-5	dec.	solid	274	63	36
	80	170-2	dec.	solid	267	24	36
	167	171-3	dec.	solid	287	38	36
	183	169-72	dec.	solid	286	48	36
CH ₃ (C ₂ H ₅)PBH ₂	3	-3 to -1	-	liquid	231	0.46	5,11
	20	118-26	dec.	solid	293	90	36
CH ₃ (C ₃ H ₇)PBH ₂	10	-	dec.	liquid	-	-	36
CH ₃ (i-C ₃ H ₇)PBH ₂	3	glass	-	liquid	182 ?	-	37
CH ₃ (C ₁₂ H ₂₅)PBH ₂	3	-	-	liquid	-	-	36
(C ₂ H ₅) ₂ PBH ₂	3	-7 to -6	340	liquid	-	-	38
(C ₆ H ₅) ₂ PBH ₂	high	263-7	dec.	solid	290	40	36
(p-CH ₃ C ₆ H ₄) ₂ PBH ₂	3	160	-	cryst. solid	375	0.56	11,38,39
(C ₆ H ₁₁) ₂ PBH ₂	3	199-203	-	cryst. solid	385	-	37,39
(CH ₂) ₄ PBH ₂	3	256-7	-	cryst. solid	484	0.22	40
(CF ₃) ₂ PBH ₂	3	169	-	cryst. solid	233	2.5	38,40
	3	30.3-30.4	176	cryst. solid	-	100	35,38
(CH ₃) ₂ PBHCH ₃	4	116	-	cryst. solid	-	-	41
(CH ₃) ₂ PB(CH ₃) ₂	3	120-32	-	waxy solid	-	-	33
C ₆ H ₅ (CH ₃)PB(CH ₃) ₂	3	333-4	326	cryst. solid	302	1.23	11,33
(CH ₃) ₂ PBF ₂	3	167-74	-	cryst. solid	304	29	36
	3	129-30	-	cryst. solid	165	100	11*

APPENDIX I (Cont'd.)

Monomer Unit	D.P.	m.p., °C.	b.p., °C.	Form at 20°C.	S.I.T., °C.	% Hydrolysis 24 hrs. at 202°C.	Ref.
(CH ₃) ₂ PEHCl	3	-	-	solid	-	-	5
(CH ₃) ₂ PBCL ₂	3 (80)	377 215-25	- dec.	cryst. solid	395	6.64	5,11*
CH ₃ (C ₂ H ₅)PBCL ₂	3	210-11	-	solid	280	84	6
(CH ₃) ₂ PEHBr	3	-	-	cryst. solid	364	-	2
(CH ₃) ₂ PBBr ₂	3	> 411 dec.	-	cryst. solid	294	99	11,43
(CH ₃) ₂ PBI ₂	3	> 411 dec.	-	cryst. solid	> 422	16.0	11
	3			cryst. solid	420	(100) ?	11
Copolymers							
$[(C_2H_5)_2PHH_2]_2[C_2H_5PHH_2]$	2+1	< -78	~330	liquid	-	-	38
$[(CH_3(C_2H_5)PBCL_2)_2CH_3(C_2H_5)PHHCl]$	2+1	-	-	waxy solid	-	-	11
$[(CH_3)_2PEHBr]_2(CH_3)_2PHH_2$	2+1	127-9	-	cryst. solid	255	-	11,39
$[(CH_3)_2PBCL_2]_2[(CH_3)_2PHHCl]_2$	2+2	-	-	cryst. solid	-	-	11
$[(CH_3)_2PEH_2]_4CH_3PHH$	4+1	98-9	-	cryst. solid	238	0.19	5,11
$[(CH_3)_2PEH_2]_5(CH_3PHH)_2$	5+2	-	-	glass	-	-	5
$[(CH_3(C_2H_5)PHH_2)_4CH_3PHH]$	4+1	-	-	viscous liquid	-	-	11
$[(CH_3(C_2H_5)PHH_2)_4C_2H_5PHH]$	4+1	-	-	viscous liquid	-	-	11
$[(CH_3(C_2H_5)PHH_2)_4C_6H_5PHH]$	4+1	-	-	glass	-	-	44
$[(CH_3)_2PBCL_2]_4CH_3PHH$	4+1	272-3	-	cryst. solid	-	-	2,5
$[(CH_3)_2PBCL_2]_5(CH_3PHH)_2$	5+2	175-85	-	solid	-	-	5
$H_2B(CH_3)P(CH_2)_3P(CH_3)BH_2$	high	-	-	solid	312	-	37
$[\overline{H_2B(CH_3)P(CH_2)_3P(CH_3)BH_2}]_x[\overline{(CH_3)_2PHH_2}]_y$	high	-	-	solid	339	-	8
$[\overline{H_2B(CH_3)P(CH_2)_3P(CH_3)BH_2}]_x[\overline{(CH_3)_2PHH_2}]_y$	4+1	121-2	-	cryst. solid	265	-	8

* This report.

APPENDIX II

CHEMISTRY OF INORGANIC POLYMER COMPONENTS

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ABSTRACT

The previously-indicated purpose of discovering new chemistry of polyvalent light elements, such as to develop a new fundamental basis for the invention of new types of thermally stable polymers, has been pursued further. As before, the work has centered about trivalent phosphorus, not only because its compounds are important to further development of phosphinoborine polymers, but also because polyphosphines offer especial promise along a number of other possible lines: for improving boron-hydride resins, for oxidation to neutral analogues of polyphosphates, for nitridation to $(Cl_2PN)_n$ analogues, and as desirable functional groups to inhibit the "unzipping" of hydrocarbon or fluorocarbon long-chain polymers. Pertinent to such ideas are the discovery of new compounds of types not previously known (R_2POPR_2 , $R_2POC_2H_4PR_2$, R_2POH , $R_2PC_2F_4PR_2$, RPC_4F_8 , $R_2PC_2H_2PR_2$, and $R_2PC_2H_2-P-C_2H_2PR_2$, for example, where R usually is CF_3) and enough exploration

R
of their chemistry to show that they actually do offer interesting possible applications to the development of polymers. There has also been progress toward knowledge of the chemistry of CH_3PCF_3 groups and toward application of diphosphines to BH-resin chemistry, as well as certain pure-research details contributing to our general working know-how for such compounds.

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CHAPTER I

PHOSPHORUS-BORON RESIN CHEMISTRY

An earlier report (Ref. 3, p. 12) described the formation of resinous products by the reaction of trimethylphosphine with pentaborane-9. In such resins the B-H ratio varied from 10:7 to 4:1 on heating from 250 to 490°C., and the ratio of B to $(\text{CH}_3)_3\text{P}$ was steadily about 5:1. High thermal stability was achieved in such resins, and interesting thermoplastic ranges were observed, but the material lacked mechanical strength and adhesiveness at ordinary temperatures. In view of the reasonable hypothesis that such resins are boron-hydride networks in which isolated $(\text{CH}_3)_3\text{P}$ units are entrapped and bonded to boron, it seemed that their mechanical strength might be improved by using a fairly strong connecting link between phosphorus atoms. Accordingly the new diphosphine $(\text{CH}_3)_2\text{PC}_2\text{H}_4\text{P}(\text{CH}_3)_2$ was employed, with an equimolar proportion of $(\text{CH}_3)_3\text{P}$, for reaction with an equimolar proportion of B_5H_9 , the purpose of the trimethylphosphine being to avoid excessive cross-linking. However, before this work is described, it will be well to present the latest information on the synthesis of $\text{P}_2(\text{CH}_3)_4$ and its use to make the ethylene-connected diphosphine.

Synthesis of Tetramethylbiphosphine. The use of the reaction $(\text{CH}_3)_2\text{PH} + (\text{CH}_3)_2\text{NP}(\text{CH}_3)_2 \longrightarrow (\text{CH}_3)_2\text{NH} + \text{P}_2(\text{CH}_3)_4$ now seems more favorable than before (Ref. 3, p. 8 and Ref. 4, p. 72), for three new experiments have shown that this reaction gives a higher yield of $\text{P}_2(\text{CH}_3)_4$ at equilibrium than had been supposed. The experiments to date are compared in Table I. In each case the components of the mixture were heated in a small sealed tube, wherein the vapor was negligible relative to the liquid.

TABLE I

Conversion of $(\text{CH}_3)_2\text{NP}(\text{CH}_3)_2$ to $\text{P}_2(\text{CH}_3)_4$

Expt. No.	Reactants (mmoles)		Time (hrs.)	Temp. (°C.)	Components of Final Mixture (total mmoles of each)				Apparent Kequil.
	Me_2PH	Me_2NPMe_2			P_2Me_4	Me_2NPMe_2	Me_2NH	Me_2PH	
1	10.58	11.05	4	62	6.83	a	a	a	2.95
	a	a	20	64	9.22	1.65	9.22	1.36	8.85
2	39.24	30.65	19	60	23.22	a	a	a	4.53
	a	+9.32	19	67	33.47	5.10	b	b	9.33
3	11.506	12.174	10,250	26	10.407	1.541	10.841	1.120	63.2
4	6.773	7.385	181	78.5	5.760	1.404	5.626	0.61	38
5	15.091	16.030	168	99.0	12.92	2.719	13.41	1.820	35

(a) Unresolved mixture, reused in the second part of the experiment.

(b) Components not separated, but estimated from the others.

Experiments 1 and 2 showed apparent equilibrium constants increasing with the extent of heating, indicating incomplete approaches toward equilibrium. Assuming that equilibrium was established in the 13.5-month experiment 3 and in the well-heated experiment 5, it would seem that lower temperatures are more favorable except for the inconvenience of low rates. But the effect of a lower temperature is not greatly advantageous in any case, for $K = 63$ implies 89% completion, while $K = 35$ means 84% completion, for equimolar proportions of the

reactants. These two values of K determine the equation $\log K = \frac{391}{T} - 0.493$,

from which K for 78.5°C. is calculated as 41.6, virtually within experimental error of the result for experiment 4, and lending support to the assumption of equilibrium in the more drastically heated case of experiment 5. This equation implies the free-energy expression $\Delta F^\circ = -1.79 + 0.00226T$ kcal.

The indicated ΔH° value of -1.79 kcal. seems to correlate with an expectation of two p-d pi bonds in $P_2(CH_3)_4$, versus only one such supplementary bond in $(CH_3)_2NP(CH_3)_2$; for it would be difficult to argue much change in the total strength of sigma bonding (P-H and N-P versus N-H and P-P). However, the value -1.79 kcal. cannot be taken as a fair measure of the importance of one p-d pi bond, for a simple comparison does not take a number of other variables into account.

Addition of the Biphosphine to Ethylene. Table II shows our present knowledge of the reaction $P_2(CH_3)_4 + C_2H_4 \longrightarrow (CH_3)_2PC_2H_4P(CH_3)_2$. Experiments 1 and 2 were reported before (Ref. 4, p. 92), while 3 and 4 represent new information.

TABLE II
Absorption of Ethylene by $P_2(CH_3)_4$
(quantities in mmoles)

Expt. No.	Reactants		Time (hrs.)	Temp. (°C.)	Recovered Reactants		Methylphosphines	
	$P_2(CH_3)_4$	C_2H_4			$P_2(CH_3)_4$	C_2H_4	$(CH_3)_3P$	$(CH_3)_2PH$
1	1.125	1.423	20	292	-	1.06	-	-
	(remainders)		72	300	-	0.77	-	-
	(remainders)		160	303	0.081	0.544	0.393	nil
2	4.417	7.616	118	207	-	6.826	-	-
	(remainders)		145	258	-	2.930	-	-
	(remainders)		120	267	1.39	2.043	0.306	0.236
3	2.59	11.31	410	280	0.28	6.49	0.490	0.134
4	5.748	13.153	760	260	0.18	6.023	1.693	nil

Expts. 1 and 2 had been done with 100 ml. bomb tubes, whereas the new Expts. 3 and 4 employed 50 ml. bomb tubes; hence the pressure of ethylene was much higher in these later runs. The data on yields of the desired diphosphine and reactants used up are presented in Table III.

TABLE III
Data Concerning Yields

Expt. No.	Reactants C ₂ H ₄	Consumed (mmoles) P ₂ (CH ₃) ₄	Reactant Ratio	Yield of mmoles	Diphosphine Percent
1	0.879	1.044	0.832	0.666	64
2	5.573	3.027	1.84	2.396	79
3	4.82	2.29	2.10	1.512	66
4	7.13	5.73	1.24	3.526	63

It appears that the destruction of ethylene actually was less than that of the biphosphine in Expt. 1, wherein the temperature was highest and the excess ethylene was least. The excess destruction of ethylene was greatest in Expt. 3, wherein the temperature was relatively high, and the pressure of ethylene also high. The delicately iodine-catalyzed Expt. 2 also showed unusual loss of ethylene relative to the yield of the desired diphosphine, but the yield of this relative to the consumed P₂(CH₃)₄ was very good.

Both Expts. 3 and 4 gave phosphine fractions fully ranging from P₂(CH₃)₄ to (CH₃)₃P in volatility and M.W., and accounting for 7.7 to 9.6% of the P in the consumed P₂(CH₃)₄. Typical was a fraction having M.W. 97.1 and vapor tension 38 mm. at 0°; but there were lighter fractions (e.g., M.W. 81.7, 89.7, or 96) which were more volatile, and some material which was only a little more volatile than P₂(CH₃)₄ (2 mm. at 0°C.). Part of such material could be explained as due to the addition of (CH₃)₂PH into ethylene to make (CH₃)₂PC₂H₅ (M.W. 90); and it might be that some P-CH₃ addition into the double bond led to P-C₃H₇ compounds also.

Characterization of the Diphosphine. Our earlier samples of (CH₃)₂PC₂H₄P(CH₃)₂ were not pure enough for satisfactory work on its physical constants. We now have distilled it under high vacuum, in a small column with reflux at 0°C., getting a main fraction which melted almost entirely in the range -1 to 0°C. The representative vapor tensions shown in Table IV determined the equation $\log_{10}P_{\text{mm}} = 6.7232 - 0.00507T + 1.75 \log_{10}T - \frac{2844}{T}$, from which the b.p. is calculated as 188.1°C. and the Trouton constant 21.00 cal./deg.mole. The new molecular weight, from the vapor density at 151°C. and 175 mm., was 152.0 (calcd., 150.1).

TABLE IV

Vapor Tensions of $(\text{CH}_3)_2\text{PC}_2\text{H}_4\text{P}(\text{CH}_3)_2$

t (°C.)	25.6	33.1	49.8	65.6	91.2	108.4	120.5	130.2
p _{mm} (obsd.)	1.05	1.69	4.69	10.97	35.68	71.0	111.2	154.0
p _{mm} (calcd.)	1.05	1.72	4.69	10.91	35.74	71.3	110.8	154.0

Synthesis of the Resin. The initial reaction, involving 2.295 mmoles of $(\text{CH}_3)_2\text{PC}_2\text{H}_4\text{P}(\text{CH}_3)_2$, 2.376 mmoles of $(\text{CH}_3)_3\text{P}$, and 2.208 mmoles of B_5H_9 , occurred during a five-hour warm-up of the mixture from -78 to 25°C . The immediate product was decidedly viscous even at 100°C ., but melted down on heating to 145°C . Its yellow tinge was barely detectable, and did not darken until the material had been heated at 320°C . Table V shows the treatment of the material and corresponding account of the vaporizable products observed.

TABLE V

Formation of the Diphosphine-Polyborane Resin

Time (hrs.)	Temp. (°C.)	Totals of Products and Recovered Reactants (mmoles)							
		H ₂	Me ₃ P	Me ₃ PBH ₃	diph.	diph. BH ₃	diph. (BH ₃) ₂	Me ₂ PH	C ₂ H ₆
1	145	0.12	0.17	1.001	-	-	-	-	-
5 16	195 244	2.85	0.82	1.459	0.085	0.107	0.204	-	-
32	320	4.73	0.92	1.459	0.085	0.107	0.204	0.108	0.166

It is interesting that so much $(\text{CH}_3)_3\text{PBH}_3$ was obtained at a medium temperature, whereas far less of the diphosphine in its various forms came out, and then only at higher temperatures. After the 244°C . heating, it was not difficult to isolate the double-BH₃ adduct $(\text{CH}_3)_2\text{PC}_2\text{H}_4\text{P}(\text{CH}_3)_2(\text{BH}_3)_2$ by high-vacuum sublimation at 150°C . (and washing-out by acetone for weighing); but the diphosphine itself and its mono-BH₃ adduct were about as volatile as the $(\text{CH}_3)_3\text{PBH}_3$ which had been formed in the same period of heating, so that a chemical method of estimation was required. The weighed fraction (0.2 to 1 mm. at room temperature) was treated with diborane, with due account taken of the amount absorbed to form the double-BH₃ adduct; then the $(\text{CH}_3)_3\text{PBH}_3$ could be sublimed off in pure form at room temperature and the weight of the double-BH₃ adduct determined. From the weight-changes and the absorption of diborane, it could be shown that both the diphosphine and its mono-BH₃ adduct had been present in calculable amounts. The double-BH₃ adduct was identified at each point of the process, by its characteristic orange-red and blue-green complementary-colored stripes when observed between crossed polaroids.

The reaction mixture at 195°C. was highly mobile at that temperature, but became immobile on cooling, showing patches of crystalline material. The 244° heating considerably increased its viscosity; for perceptible flow under gravity, a temperature near 150°C. was required. At room temperature, the non-volatile part could be pulverized by shaking the sealed tube. After the 320°C. heating, the resin appeared like peanut-brittle in which bubbles had blown out. It did not flow at 320°C., but it adhered strongly to the Pyrex wall even after cooling to -196°C. It was obvious that its self-adhesiveness was superior to that of earlier resins; and it was quite noticeably more difficult to break it under stress.

The yield of non-volatile material agreed reasonably well with that calculated from the stoichiometry: about 335 mg. This included some 7 to 10% of acetone-extractable gum. The over-all empirical formula was $\sqrt{B_{81}H_{36}diph_{13}(Me_2P)_2}_x$, obtained by taking account of the small yields of $(CH_3)_2PH$ and C_2H_4 in terms of an attack by B-H bonds upon the P-C₂H₄-P bonding. This tendency toward formation of $(CH_3)_2P-B$ bonds, and probably P-C₂H₄-B bonds also, may be useful in developing more cross-links at higher temperatures.

The ratio of B to P in this resin was only about 2.9 to 1, considerably lower than observed in the earlier $(CH_3)_3P-B-H$ resins (about 5 to 1). The reason very probably is that many of the diphosphine units held BH_3 groups at one end while the other end was incorporated in the B_xH_y polymer network. Hence it will be important to seek stronger means of removing BH_3 groups, in order to tie both ends of the diphosphine into the polymer network. It is apparent that substantially no $(CH_3)_3P$ remained in the resin, but the question whether a larger proportion of it will pull out more of the BH_3 groups, letting more of the diphosphine act bifunctionally toward the B_xH_y polymer, must be answered in the next experiment on this subject.

Attempts to Make a Trifluoromethyl-thiophosphine. The easy synthesis of H_2NSCF_3 of (Ref. 1, p. 41) and $(CH_3)_2NSCF_3$ (Ref. 4, p. 107) suggested the possibility of making a $(CH_3)_2PSCF_3$, which might have value for making resins from B_5H_9 . However, all experiments directed toward such a synthesis have failed. In one case nearly equimolar amounts of $(CH_3)_2PH$, CF_3SCl , and $(C_2H_5)_3N$ were warmed together from -196 to -78°C., forming a white solid. This turned brown on warming to room temperature, giving nothing volatile except a trace of what seemed to be CF_3SH . The same components in ether gave similar results.

The next attempt used 3.07 mmoles of CF_3SSCF_3 with 15.24 mmoles of $(CH_3)_2PH$. The mixture reacted vigorously on warming to -30°C., forming a non-volatile sirupy liquid. After 3.91 mmoles of $(CH_3)_2PH$ had been recovered, there remained a volatile product (M.W. 105; v.t. 0.7 mm. at -78°C.), which decomposed to dark material at room temperature. It is conceivable that the CF_3S unit has too much oxidizing power to be attached to trivalent phosphorus.

CHAPTER II

FURTHER CHEMISTRY OF THE C_4H_8P RING

Synthesis of the Chlorophosphine. The earlier work on the conversion of the amino-cyclo-phosphine $(CH_3)_2NPC_4H_8$ to the chlorophosphine C_4H_8PCl (WADC TR 56-82, Pt. II, pp. 7-8) was unsatisfactory because it was done before the necessary precautions had been discovered by a study of the reaction of $(CH_3)_2NP(CH_3)_2$ with HCl . The reaction $(CH_3)_2NPC_4H_8 + 2HCl \longrightarrow (CH_3)_2NH_2Cl + C_4H_8PCl$ now has been repeated, using a slightly deficient proportion of HCl because any excess would have been difficult to remove from the product. The strong solubility of HCl in the chlorophosphine was demonstrated in a separate experiment, which seemed to indicate the presence of an unstable hydrochloride of the chlorophosphine at low temperatures.

Just as in the parallel synthesis of $(CH_3)_2PCl$,⁵ the reaction was carried out in a temperature range of -100 to $25^\circ C.$, in a plain 50 ml. reaction tube jointed to a stopcock leading to the high-vacuum system. For such experiments it has been found advantageous to distil the immediate product to a second reaction tube, heating the solid residue to $100^\circ C.$ to drive out any aminophosphine which failed to react through capture by the solid or because of the formation of a complex with the chlorophosphine. Thus the reaction could be completed only by repeating the back-and-forth distillation three or four times, until there was no further formation of the non-volatile solid.

In one such experiment, 197.0 mg. (1.502 mmoles) of $(CH_3)_2NPC_4H_8$ and 2.931 mmoles of HCl produced a highly uniform volatile liquid weighing 165.8 mg. Taken as pure C_4H_8PCl (1.353 mmole), this represents a 92.3% yield based upon the HCl directly; or, considering that the excess aminophosphine would form a 1:1 complex with the chlorophosphine, the yield of the chlorophosphine would be 94.8% of the calculated value.

Properties of the Chlorophosphine. This chlorophosphine formed a glass at $-78^\circ C.$ so that its melting point could not be observed. Exactly like $(CH_3)_2PCl$, it slowly formed a buff-colored torch-sublimable solid on contact with mercury. The reaction seemed not to form any mercury compound, but probably was a catalytic disproportionation. This effect of mercury made it difficult to determine the molecular weight or to get dependable vapor-tension values at elevated temperatures; however, molecular weights of 123.9 and 124.1 (calcd. 122.5) were obtained on samples at $100^\circ C.$ and 50-80 mm. Two fairly dependable vapor-tension values were 3.4 mm. at $23.4^\circ C.$ and 42.5 mm. at $71.8^\circ C.$ The corresponding equation ($\log_{10} p_{mm} = 8.357 - 2321/T$) would give the Trouton constant as 25.0 cal. per deg.mole, suggesting that the $\log p$ vs. $1/T$ line curves toward a higher boiling point than the $151^\circ C.$ value implied by the equation. Using a linear extrapolation from the higher vapor tension value, with the assumption that the real Trouton constant is the normal 21.0, the b.p. is estimated as $165^\circ C.$

The Reconversion to the Aminophosphine. The reaction $C_4H_8PCl + 2(CH_3)_2NH \longrightarrow (CH_3)_2NH_2Cl + (CH_3)_2NPC_4H_8$ could not be done quantitatively in a vacuum system involving mercury and stop-cock grease, on account of side reactions probably related to disproportionation. However, even reactions such as $4C_4H_8PCl \longrightarrow C_4H_8PC_4H_8PC_4H_8 + Cl_2PC_4H_8PCl_2$ or $2C_4H_8PCl \longrightarrow Cl_2PC_4H_8PC_4H_8$ would not alter the number of P-Cl bonds, so that the amine treatment led to a correct analysis for chloride.

A 106.7 mg. sample of C_4H_8PCl was treated in a weighing bulb with excess dimethylamine, producing 72.3 mg. (0.551 mmole, or 60% yield) of $(CH_3)_2NPC_4H_8$ and a non-volatile solid. The low yield of the aminophosphine could be explained by the presence of a liquid which distilled under high vacuum only when heated at least to $100^\circ C$. The non-volatile solid (weighing 5% more than expected because of unremoved by-product) was dissolved in water, neutralized to methyl red by slight addition of sodium hydroxide, and titrated by the adsorption-indicator method to show 0.89 mmole of Cl^- (calcd., 0.87).

A manuscript presenting all of our work on the C_4H_8P ring compounds has been accepted for publication in the Journal of the American Chemical Society, where it is expected to appear in February, 1960

CHAPTER III

OXYPHOSPHINE CHEMISTRY

The P-O-P linkage is important in the chemistry of pentavalent phosphorus, especially in various polymeric situations. For trivalent phosphorus, however, such a linkage seems not to have been reported. Probably one reason is the ease with which many RO- substituted phosphines rearrange into the corresponding phosphine oxides. Now just such a rearrangement has a special interest for polymer chemistry because this is one way in which a monomeric glycoxy-phosphine can change into a polymeric phosphinic anhydride of potentially high thermal stability (Ref. 4, p. 103).

As a step toward understanding such reactions, we now have made the first diphosphoxane, $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$, and studied some of its chemical consequences. However, the corresponding methyl compound, $(\text{CH}_3)_2\text{POP}(\text{CH}_3)_2$, could not be made by similar means - possibly on account of rearrangement to a non-volatile phosphine oxide and secondary changes thereafter. Apparently this type of rearrangement is either inhibited or prevented altogether by strongly electronegative groups such as CF_3 on phosphorus.

Synthesis and Physical Properties of the Diphosphoxane

The Iodide-Silver-Carbonate Method of Synthesis. Initial experiments showed that the reaction $2(\text{CF}_3)_2\text{PI} + \text{Ag}_2\text{CO}_3 \longrightarrow \text{CO}_2 + 2\text{AgI} + (\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ proceeds in a satisfactory manner at room temperature but the purity of the phosphoxane was somewhat disturbed by the action of vacuum-line mercury upon the $(\text{CF}_3)_2\text{PI}$ to form $\text{P}_2(\text{CF}_3)_4$. This could not be removed by the usual high-vacuum distillation methods because of its very similar volatility (b.p. only about 5° higher). For this reason a mercury-free high-vacuum manifold was constructed, so that the synthesis could be done with the materials in contact only with Pyrex glass and chlorofluorocarbon stop-cock grease.

A 15.9 mmole sample of $(\text{CF}_3)_2\text{PI}$ (4.731 g.; 44.0 mm. at 0°C ., demonstrating purity) was shaken with carefully dried silver carbonate until the formation of carbon dioxide virtually ceased. The treatment was repeated three times, with fresh silver carbonate. The residual $(\text{CF}_3)_2\text{PI}$ (1%) could not be separated from the diphosphoxane by distillation methods, but was easily converted to $(\text{CF}_3)_2\text{PCL}$ by reaction with silver chloride. Then the diphosphoxane was purified by allowing it to pass at minimal pressure through a trap at -45°C . and condense in a -78°C . trap, through which the $(\text{CF}_3)_2\text{PCL}$ was removed. The $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ amounted to 6.27 mmoles, or a yield of 79%. No volatile by-products could be observed. Higher, but less accurately measured, yields were obtained in other experiments wherein there was more persistent repetition of the Ag_2CO_3 treatment. In one case the $(\text{CF}_3)_2\text{PI}$ was allowed to flow over a bed of silver carbonate, with possibly some gain in convenience, but no advantage in regard to yield.

The new compound $(\text{CF}_3)_2\text{PBr}$ (Chapter III) was treated once with Ag_2CO_3 , with 13% conversion to the desired diphosphoxane - somewhat less than the iodide gave under similar conditions. With HgO liquid $(\text{CF}_3)_2\text{PBr}$ began to react within three minutes, but the highly exothermic process gave scarcely any volatile product. It is possible that the HgO supplied oxygen to form a $=\text{P}-\text{O}-\text{P}=$ structural unit. In

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fact, when $(\text{CF}_3)_2\text{PBr}$ vapor was passed over a bed of HgO , some $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ was formed, but disappeared along with the $(\text{CF}_3)_2\text{PBr}$ as the passage was repeated. When all of the volatile material had been consumed, the tube was heated, yielding droplets of mercury and a white sublimate which might well have been the phosphinic anhydride $[(\text{CF}_3)_2\text{PO}]_2\text{O}$.

Volatility and M.P. of the Diphosphoxane. The melting range of pure $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ was observed as -53.1 to -52.6°C . Its vapor tensions, shown in Table VI, determined the equation $\log_{10}P_{\text{mm}} = 6.1276 - 0.005092T + 1.75 \log_{10}T - 2078.5/T$, according to which the normal boiling point is 78.3°C . and the Trouton constant is $22.0 \text{ cal./deg.mole}$.

TABLE VI

Vapor Tensions of $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$

t ($^\circ\text{C}$.)	P_{mm} (obsd.)	P_{mm} (calcd.)	t	p (obsd.)	p (calcd.)
-14.9	9.64	9.69	24.2	89.5	89.6
-11.7	12.01	11.97	37.7	166.7	166.3
-5.1	18.2	18.2	43.5	212.8	212.9
0.0	24.4	24.6	52.0	299.8	299.6
10.8	45.4	45.3	61.1	421.8	420.7

Proof of the Diphosphoxane Formula. The molecular weight of the pure diphosphoxane was determined in the vapor phase, as 354.2 ; calcd., 354.0 . A basic hydrolysis of a 42.0 mg . sample at 100°C . yielded 32.7 mg . of HCF_3 (mol. wt. 70.0 , as calcd.), corresponding to 3.94 CF_3 groups per molecule of $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$. Further evidence of the constitution of the diphosphoxane is its nearly quantitative reaction with HCl to form $(\text{CF}_3)_2\text{POH}$ and $(\text{CF}_3)_2\text{PCl}$, as described later in this chapter. This reaction correlates with the P-O-P linkage, which is more satisfactorily demonstrated by the infra-red spectrum.

Absorption Spectra of the Diphosphoxane. Considerable work has been done by different research groups, toward identifying the infra-red absorption characteristics of the P-O-P linkage in pyrophosphates.⁸ After some initial claims and counterclaims there now is general agreement that the vibration occurs in the $910\text{--}970 \text{ cm}^{-1}$ region for organo-pyrophosphates and pyrophosphate polymers. In the present case, however, the P-O-P link would occur with trivalent phosphorus, with no ambiguity in regard to the assignment of an intense band at 925 cm^{-1} to the asymmetric P-O-P stretching vibration. The symmetric vibration for a bent P-O-P bond should occur very weakly at a lower frequency; or for a linear P-O-P bond it should be inactive. There was no doubt in the assignment of the other vibrations which are summarized in Table VII along with the frequencies observed for $\text{P}_2(\text{CF}_3)_4$. These numbers are rounded off to the nearest 5 cm^{-1} .

TABLE VII

Vibration Frequencies of $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ and $\text{P}_2(\text{CF}_3)_4$

$(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$	$\text{P}_2(\text{CF}_3)_4$	Intensity	Assignment
1230	1200	vs	C-F Stretching
1185	1170	vs	
1145	1145	vs	
-	1120	vs	
950	-	s	P-O-P Stretching
925	-	vs	
885	-	m	
755	745	m	C-F Bond
715	-	m	

The ultra-violet spectrum of the diphosphoxane showed only a single maximum, at 2110 Å. (mol. ext. coeff., 3580), with the corresponding minimum centered at 1965 Å. ($\epsilon = 650$). The strong maximum would correspond to a three-atom traverse by the oxygen 2p electrons; however, the usual electron-in-a-box theory is not fully applicable because it would require a triplet state due to degeneracy of the $n = 1$ electronic level, or else a splitting of levels to give at least two peaks. Actually the peak is very smooth and symmetrical. Presumably a relatively strong assignment of the pertinent electrons to oxygen makes the simple box theory inadequate.

Chemical Behavior of the Diphosphoxane

Thermal Stability and Decomposition. The diphosphoxane $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ was heated for 66 hours at 150°C. without any noticeable decomposition, but at 250°C. a sample was about 25% decomposed during 60 hours. A somewhat larger sample (0.978 mmole) was virtually all decomposed during 14 days at 250°C., yielding 0.490 mmole of CO (proved by CuO combustion), 0.682 mmole of PF_3 , 0.850 mmole of $(\text{CF}_3)_2\text{PF}$, 0.294 mmole of $(\text{CF}_3)_3\text{P}$, and 40.4 mg. of an unresolved mixture containing CF_3 groups, P-O-P units, and P-F bonds. The involatile residue was black and presumably contained either trivalent or elementary phosphorus (or both), for it changed visibly on contact with air.

Electron-Donor-Acceptor Character. The diphosphoxane has no more than the weakest base character, for a sample of it was quite inert toward boron trifluoride; the mixture was slowly warmed from -196°C. to -5°C. (18 hours) without any evidence of adduct formation. The boron trifluoride was recovered without loss. Sulfur dioxide also proved quite inert toward the diphosphoxane, during 3 hours at room temperature. Both of these electron-acceptors might have been expected to undergo metathesis reactions with the diphosphoxane, if initial adduct formation had been possible. It is apparent that the base character usually expected of ether-like oxygen, or of trivalent phosphorus, has been most severely diminished by the CF_3 groups on phosphorus.

On the other hand, the diphosphoxane has a very definite electron-acceptor character, as demonstrated by its formation of an adduct with trimethylamine. The existence of the adduct $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2 \cdot (\text{CH}_3)_3\text{N}$ was demonstrated by a pressure-composition isotherm at -78.5°C. The solid diphosphoxane absorbed the amine only very slowly at that temperature, but good adduct-formation was achieved by warming the mixture to -50°C. (just above the melting point). Then the mixture was cooled back to -78.5°C. and equilibrated for 15-20 minutes before each pressure reading. The data, showing a sharp increase of pressure above one $(\text{CH}_3)_3\text{N}$ per phosphoxane, are presented in Table VIII. The diphosphoxane sample amounted to 0.202 mmole, showing zero pressure at -78.5°C. before treatment with the amine.

TABLE VIII

The System $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2 \cdot (\text{CH}_3)_3\text{N}$ at -78.5°C.

Mmoles Amine	0.130	0.176	0.192	0.198	0.202	0.271	0.342	0.403
Ratio of Amine to $(\text{CF}_3)_4\text{P}_2\text{O}$	0.647	0.875	0.955	0.985	1.000	1.349	1.700	2.005
p (mm.)	0.04	0.04	0.04	0.05	0.04	0.89	1.00	1.14

The amine pressures above the 1:1 composition are well below the value for the pure amine (about 8 mm. at -78.5°C.), but they are not near enough to constancy to demonstrate a real attachment of a second molecule of amine. A solid solution effect seems to be indicated.

The stability of the 1:1 adduct is represented by the dissociation pressures shown in Table IX. These data were taken at constant temperatures (held mostly by slush-baths), with measurement by a micrometer slide cathetometer. They are correlated by the equation $\log_{10}P_{\text{mm}} = 8.752 - 1979/T$, from which one might calculate t for 760 mm. as 63.5°C. , except that the substance could not retain its identity much above -20°C. It is also not possible to convert this equation into a valid free-energy expression, for a measurement of the component vapors at 23.9°C. showed that the dissociation into these components was only 81% complete under the conditions of the experiment (ave. mol. wt. 229.6 vs. 206.5 for complete dissociation).

TABLE IX

Dissociation Pressures of $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2 \cdot (\text{CH}_3)_3\text{N}$

t (°C.)	-78.5	-63.5	-45.3	-30.6	-23.2
p_{mm} (obsd.)	0.04	0.22	1.13	3.92	6.85
p_{mm} (calcd.)	0.04	0.21	1.17	3.92	6.84

This fairly weak but definite attachment of trimethylamine to a PX_3 compound apparently is to be expected when X represents highly electronegative groups; indeed the adduct $\text{PF}_3 \cdot (\text{CH}_3)_3\text{N}$ was observed in these laboratories many years ago. However, the electron-acceptor strength of phosphorus in $\text{P}_2(\text{CF}_3)_4$ evidently is insufficient for this diphosphine to form a trimethylamine adduct, for this amine failed to react with $\text{P}_2(\text{CF}_3)_4$ at room temperature, and could be distilled away completely at -78°C .

Addition of the Diphosphoxane to Ethylene. The initial reason for bringing the diphosphoxane $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ into contact with ethylene was a desire to free an early sample from the impurity $\text{P}_2(\text{CF}_3)_4$, which easily adds to ethylene to form a considerably less volatile diphosphine (Ref. 4, p. 91). However, the diphosphoxane itself reacted with ethylene at a similar rate per mole, so that the purity of the remaining diphosphoxane was scarcely improved. For a more direct study of this addition at a convenient rate, the temperature was raised to 80°C .; then after 16 hours the 2.06 mmole sample of crude diphosphoxane had used up 2.11 mmoles of the initially present 2.59 mmoles of ethylene. However, the process was not simply an addition to form $(\text{CF}_3)_2\text{POC}_2\text{H}_4\text{P}(\text{CF}_3)_2$, for a major part (0.675 mmole) of the mixture was a fraction (not resolvable by distillation methods) in which the infra-red spectrum showed a considerable proportion of unused diphosphoxane, and the yield of $(\text{CF}_3)_2\text{POC}_2\text{H}_4\text{P}(\text{CF}_3)_2$ was only 0.368 mmole, or 19.6% of the phosphoxane actually present at the start. This was estimated from the yield of $(\text{CF}_3)_2\text{PC}_2\text{H}_4\text{P}(\text{CF}_3)_2$ (0.181 mmole, representing 9% diphosphine in the original diphosphoxane). The by-products included 0.197 mmole of $(\text{CF}_3)_3\text{P}$ and at least 101 mg. of an extremely viscous involatile material which did not form crystals even on cooling to -196°C . An attempt to determine the molecular weight of this viscous product by its effect on the vapor tension of ether did not succeed because it reacted with the solvent. In view of the excess consumption of ethylene in the main reaction, this might include a double ethylene adduct such as the ether-like $(\text{CF}_3)_2\text{PC}_2\text{H}_4\text{OC}_2\text{H}_4\text{P}(\text{CF}_3)_2$, or polymeric material involving a lengthened hydrocarbon chain.

The 0.368 mmole sample of $(\text{CF}_3)_2\text{POC}_2\text{H}_4\text{P}(\text{CF}_3)_2$ was easily purified, for it proved to far less volatile than the accompanying bis-phosphino-ethane. Its molecular weight, 381.9, supported the assumed formula (calcd., 382.0); and the basic hydrolysis of a later, somewhat less purified sample indicated four CF_3 groups for the molecule. The purity of the present sample was indicated by its 0.2° melting range at 5.0°C . and by the consistency of the vapor tensions shown in Table X. These results are correlated by the simple equation $\log_{10} p_{\text{mm}} = 7.598 - 2240/T$; b.p. 201.7°C . and Trouton constant $21.6 \text{ cal./deg.mole}$.

TABLE X

Vapor Tensions of $(CF_3)_2POC_2H_4P(CF_3)_2$

t (°C.)	0.0	14.1	19.8	26.6	38.0	49.7	54.9	63.2
p _{mm} (obsd.)	0.23	0.64	0.88	1.35	2.54	4.68	6.11	8.60
p _{mm} (calcd.)	0.25	0.63	0.89	1.34	2.53	4.60	5.92	8.69
t (°C.)	66.1	71.1	75.0	76.0	80.3	89.8	90.1	94.0
p _{mm} (obsd.)	9.95	12.3	14.9	15.4	18.3	26.7	27.1	31.4
p _{mm} (calcd.)	9.91	12.4	14.7	15.3	18.4	26.8	27.2	31.5

In a second experiment on the addition of the diphosphoxane to ethylene, the sample was virtually free of $P_2(CF_3)_4$ but the results were no less complex. The reactants (1.142 mmoles of the diphosphoxane and 1.105 mmoles of ethylene - the latter in deficient proportion to minimize chain-lengthening) were kept at 58°C. for 40 hours, with only 25% consumption of the C_2H_4 . After 16 hours at 100°C., 55% (0.608 mmole) of the C_2H_4 was gone. Half of the diphosphoxane could be recovered, with impurities such that the average molecular weight was 322 (pure, 354), and only 3.25 HCF_3 per mole formed by basic hydrolysis. The contaminants included C-H bonds, as shown by the deformation peaks in the infra-red spectrum (1395 and 1465 cm^{-1}). The earlier experiment led to more of this, and a lower average M.W. (294). In the present case there were numerous minor reaction products, including 5% of the consumed $(CF_3)_2P$ units in the form of $(CF_3)_3P$. This would mean that CF_3P units no doubt were present in the by-products, which might include the ring-monomer and low polymers of the $CF_3P-C_2H_4$ - unit. A solid melting in the range 90-95°, subliming slowly under high vacuum at that temperature, was converted by BF_3 to involatile liquid material. It is estimated that the yield of the beta-phosphino-ethoxyphosphine $(CF_3)_2PC_2H_4OP(CF_3)_2$ did not exceed 15%.

By comparison with the conditions and results of the earlier experiment, it is apparent that the formation of this phosphino-ethoxy-phosphine is considerably more difficult when $P_2(CF_3)_4$ is absent. Hence it becomes interesting to speculate on the question why $P_2(CF_3)_4$ seems to aid the addition of the diphosphoxane to ethylene. It is not difficult to argue that the electron donor and acceptor properties of the P atoms in $P_2(CF_3)_4$ make it easy for it to add to the pi bond of ethylene, but that there is no very easy mechanism whereby a P-O bond in the diphosphoxane would break to go into ethylene - for the O atom here is no electron acceptor and surely a very poor donor. It is possible that $P_2(CF_3)_4$, in the process of adding to ethylene, generates stronger donor and acceptor units which attack the diphosphoxane to make it effectively reactive. But there is not yet any real basis for understanding the possible mechanisms.

A more direct synthesis of $(CF_3)_2PC_2H_4OP(CF_3)_2$ was sought through addition of $P_2(CF_3)_4$ to ethylene oxide, but the only result was polymerization of the

ethylene oxide. Even when the ethylene oxide was slowly admitted as a gas into a large bulb containing $P_2(CF_3)_4$ (entering from below to improve mixing), virtually all (98.4%) of the $P_2(CF_3)_4$ was recovered after four hours at room temperature. Three-fourths of the ethylene oxide went to form a polymer-film on the walls of the bulb.

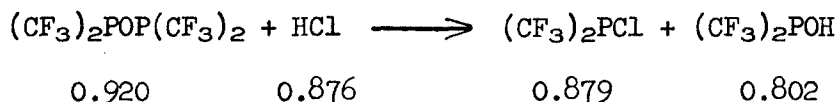
Bis(Trifluoromethyl)Phosphinous Acid

It has generally been assumed that a true phosphinous acid, R_2POH , is incapable of stable existence, tending to rearrange very quickly to the secondary phosphine oxide, which soon would disproportionate: $2R_2HPO \rightarrow R_2PH + R_2POOH$.^{7,8} Numerous esters of phosphinous acids are known (although they are somewhat unstable in regard to rearrangement to phosphine oxides), but the only reported phosphinous acids are those in which there is a nitrogen-base atom available either to receive a proton from the P-OH part or to form a hydrogen bond with it.⁹ However, we find that when R is CF_3 , the phosphorus atom has too little base strength to receive the proton from oxygen, and so the phosphinous acid $(CF_3)_2POH$ is stable and has no apparent tendency to rearrange. Furthermore, our diphosphoxane $(CF_3)_2POP(CF_3)_2$ provides a very easy route to its synthesis.

Splitting of the Diphosphoxane by HCl. In an exploratory experiment 0.594 mmole of $(CF_3)_2POP(CF_3)_2$ and 0.830 mmole of HCl were heated together in a sealed tube (68 hrs.; $100^\circ C.$) to give 0.545 mmole of $(CF_3)_2PCL$ and 0.453 mmole of $(CF_3)_2POH$. The same mixture was heated a further 40 hours at $100^\circ C.$, increasing the yield of $(CF_3)_2PCL$ to 0.611 mmole and lowering the yield of $(CF_3)_2POH$ to 0.411 mmole. The fraction representing the unused HCl contained a denser gas - probably HCF_3 . It seemed that the main reaction was $(CF_3)_2POP(CF_3)_2 + HCl \rightarrow (CF_3)_2PCL + (CF_3)_2POH$; but if the mixture was heated too long, the secondary reaction $(CF_3)_2POH + HCl \rightarrow (CF_3)_2PCL + HOH$ became possible, with removal of the water for an attack producing fluoroform. For better yields, then, a more delicate process was required.

In the preliminary experiment it was noticed that the desired phosphinous acid was strongly absorbed by the usual stop-cock greases but appeared to be stable in the presence of mercury. Accordingly the latter experiments were done by sealing off the reactants in Pyrex tubes provided with magnetic break-off tips. When small losses could be tolerated, it was possible to use the more orthodox mechanical tube-opener with a shellac-base vacuum wax ("Varno") to seal in the tube-tip. Even then it was necessary to send the vapor past the seal at a low pressure, and to recover what was absorbed, by high-vacuum passage to a trap at $-196^\circ C.$ during an extended time. It was also found that $(CF_3)_2POH$ usually was underestimated as a gas, apparently on account of a strong self-interaction which might be ascribed to van der Waals forces or hydrogen bonding.

In the absence of grease, then, $(CF_3)_2POH$ was obtained in 91.6% yield by the following reaction (check values in mmoles):



This result was obtained by heating the reactants for 86 hours at $100^\circ C.$, and was sufficiently near to quantitative for use as an argument for the formula $(CF_3)_2POH$.

Physical Properties of the Phosphinous Acid. A highly purified sample of $(\text{CF}_3)_2\text{POH}$ melted in the range -21.3 to -21.1°C . The vapor-phase molecular weight determination was difficult because the vapor-phase contraction effect made it hard to get good estimates of the standard volume and the strong tendency of stop-cocks to trap the vapor led to a tendency toward losses of weight. The most dependable result was 184.8; calcd., 186.0.

The purity of the compound was indicated not only by its sharp melting point, but also by the conformity of its vapor tensions to the usual rules. For the solid (Table XI), the equation is $\log_{10}p_{\text{mm}} = 10.7217 - 2426.1/T$; and for the liquid (Table XIa), $\log_{10}p_{\text{mm}} = 9.6968 - 0.01099T + 1.75 \log_{10}T - 2528.3/T$. The latter equation gives the normal b.p. as 61.4°C . and the Trouton constant as 21.4 cal./deg.mole. The high value of the coefficient of T in the Nernst equation, meaning an abnormally large curvature in the $\log p$ vs. $1/T$ line, can be attributed to hydrogen bonding, the effect of which diminishes with rising temperature. The two equations together give the m.p. as -20.8°C ., in good agreement with observation. Calculation of the enthalpy of vaporization at that temperature (from each equation) gives the molar enthalpy of fusion as 1910 cal.

TABLE XI

Vapor Tensions of Solid $(\text{CF}_3)_2\text{POH}$

t ($^\circ\text{C}$.)	-39.4	-35.7	-34.8	-28.1	-27.0	-23.4	-21.5	-21.1
p_{mm} (obsd.)	2.19	3.38	3.55	6.63	7.34	10.30	12.10	12.57
p_{mm} (calcd.)	2.19	3.28	3.51	6.65	7.37	10.22	12.10	12.53

TABLE XIa

Vapor Tensions of Liquid $(\text{CF}_3)_2\text{POH}$

t ($^\circ\text{C}$.)	-16.3	-12.3	-4.5	0.0	8.1	10.6	14.1	15.3
p_{mm} (obsd.)	17.75	23.34	38.5	50.6	80.8	91.6	110.2	116.6
p_{mm} (calcd.)	17.74	23.32	38.5	50.6	80.1	91.6	110.1	116.9

Absorption Spectra of the Phosphinous Acid. The best evidence of the presumed $(\text{CF}_3)_2\text{POH}$ structure of the phosphinous acid is its gas-phase infra-red spectrum. The O-H stretching vibration is evident from a band at 3670 cm^{-1} . Moreover, the absence of any peak in the region characteristic of P-H stretching (around 2300 cm^{-1}) is a direct argument against the phosphine-oxide structure $(\text{CF}_3)_2\text{HPO}$. Peaks at 1215, 1160, and 1125 cm^{-1} clearly show the multiplicity of C-F stretching

which is characteristic of two CF_3 groups on one phosphorus atom, while a band centered at 745 cm^{-1} is assigned to a C-F deformation vibration. Two other strong bands at 1060 and 860 cm^{-1} are tentatively assigned to P-OH and P=O deformations, respectively.

Taken with other knowledge of the compound, including the nearly quantitative synthesis and the molecular weight, the conformity of the infra-red spectrum to expectations leaves no doubt of the identity of the compound as $(\text{CF}_3)_2\text{POH}$.

The ultraviolet spectrum of this compound showed a peak at 2025 \AA . and a minimum near 1900 \AA ., with respective molar extinction coefficients 1275 and 350 . This is a reasonable spectrum for a P-O bond.

The Question of Rearrangement. Although the infra-red spectrum of this phosphinous acid demonstrated an O-H but no P-H bond, the possibility of a movement of H from O to P was not excluded. It could be argued that a proton on oxygen usually is fairly mobile, so that the phosphine oxide form $(\text{CF}_3)_2\text{PHO}$ should have formed if it were stabler than the $(\text{CF}_3)_2\text{POH}$ form; and in any case it would be difficult to argue a stronger base-action by the lone-pair electrons of P than for O in $(\text{CF}_3)_2\text{PO}^-$. However, it has been demonstrated (Ref. 3, p. 33) that the tert.-butyl phosphinite $(\text{CF}_3)_2\text{POC}_4\text{H}_9$ can be rearranged to the phosphine oxide form by the action of phosphoric anhydride. Accordingly, a sample of $(\text{CF}_3)_2\text{POH}$ was passed four times over a bed of phosphoric anhydride, and then exposed for a week to a small proportion (9 mole percent) of water; after such exposure, it was recovered quantitatively without change of properties. It seems reasonable to assume that the $(\text{CF}_3)_2\text{POH}$ form is stable, whereas $(\text{CF}_3)_2\text{C}_4\text{H}_9\text{PO}$ owes its stability to a P-C bonding character different from a P-H bond.

Protic-Acid Character. In an exploratory experiment, 0.215 mmole of $(\text{CH}_3)_3\text{N}$ was absorbed by 0.215 mmole of $(\text{CF}_3)_2\text{POH}$, to form a white solid from which no vapor could be obtained at room temperature. The sample melted in the range $44-46^\circ\text{C}$. and then had a wider melting range - as though some important internal reorganization had occurred. It now absorbed an equimolar amount (0.217 mmole) of HCl , but the expected $(\text{CF}_3)_2\text{POH}$ could not be recovered. Thus it appeared either that a rearrangement actually had occurred, or that HCl was too weak to displace the phosphinous acid, presumably attaching itself to P as a result of an amine-induced base strength at that point. The latter hypothesis seems to be contradicted by the following experiment, wherein the amine-adduct was treated more gently.

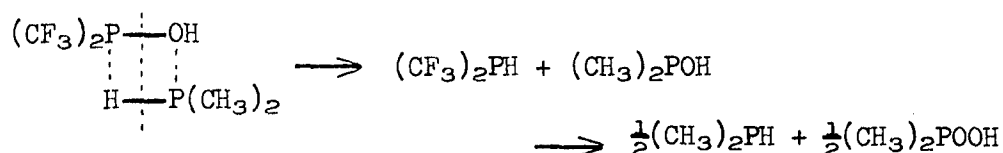
In this new experiment, the adduct was made again, from a sample of $(\text{CF}_3)_2\text{POH}$ (apparently 0.200 mmole , but probably underestimated) which absorbed 0.232 mmole of $(\text{CH}_3)_3\text{N}$. The reaction took place at a low temperature, and the sample was warmed to room temperature only just before treatment with excess HCl , of which 0.232 mmole was absorbed. The reaction was signalled by an immediate change from a white solid to a viscous liquid. Then by a prolonged and relatively arduous process of repeated vacuum distillations at room temperature it was possible after three days to recover 82% of the expected $(\text{CF}_3)_2\text{POH}$. Part of the loss would correlate with a 10% yield of $(\text{CF}_3)_2\text{PCl}$; and since this meant that some water was formed, the difficulty of removing $(\text{CF}_3)_2\text{POH}$ from this water also could account for some loss. There was also a 2% yield of HCF_3 . The main bulk of the non-volatile white solid was assumed to be $(\text{CH}_3)_3\text{NHCl}$.

Thus, it appears that the original adduct was the salt $(\text{CH}_3)_3\text{NH}^+(\text{CF}_3)_2\text{PO}^-$, and that $(\text{CF}_3)_2\text{POH}$ behaved as a weaker acid than HCl ; however the extreme difficulty

of isolating the liberated $(\text{CF}_3)_2\text{POH}$ was not obviously intelligible. In general, this compound has proved difficult to work with in a quantitative manner because it is strongly absorbed by our stop-cock greases and vacuum waxes; and it is quite possible that it was hydrogen-bonded to $(\text{CH}_3)_3\text{NHCl}$, either in the $\text{N}-\text{H}---\text{O}$ manner or the weaker $\text{O}-\text{H}---\text{Cl}$ way, or both.

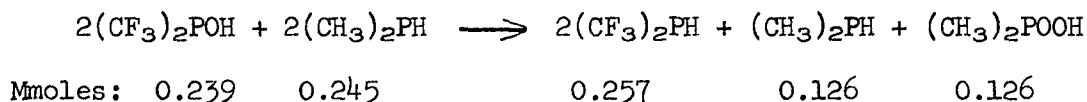
An attempt to recheck the ammonium-salt character of $(\text{CF}_3)_2\text{POH} \cdot (\text{CH}_3)_3\text{N}$ by the infra-red spectrum of a KBr pellet, failed because the highly hygroscopic character of the material made the spectrum unreliable.

The Reaction with Dimethylphosphine. The hydrolysis $(\text{CH}_3)_2\text{P}-\text{P}(\text{CF}_3)_2 + \text{HOH} \rightarrow (\text{CF}_3)_2\text{PH} + "(\text{CH}_3)_2\text{POH}"$ (Ref. 4, p. 87) could not be understood in terms of the obvious expectation that oxygen would attach to the more electronegative $\text{P}(\text{CF}_3)_2$ group and hydrogen to the more basic $(\text{CH}_3)_2\text{P}$ group, unless it were assumed that any early formation of $(\text{CF}_3)_2\text{POH}$ and $(\text{CH}_3)_2\text{PH}$ would be followed quickly by a redox type of exchange of H for OH:



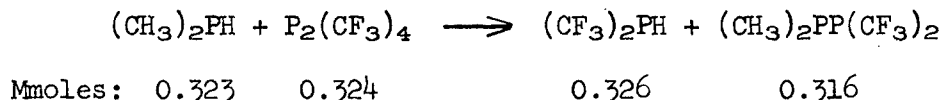
The initial attempts to test this hypothesis failed for lack of the right experimental conditions, partly because the plan of the experiment was based upon the literature belief that $(\text{CF}_3)_2\text{POH}$ would be too unstable to be isolated and tried directly with dimethylphosphine.

We now have made a direct test of the reaction of $(\text{CF}_3)_2\text{POH}$ with $(\text{CH}_3)_2\text{PH}$ under anhydrous conditions, and found that equimolar proportions of these reactants do indeed undergo the postulated exchange quantitatively at room temperature:



As usual, the phosphinous acid was somewhat underestimated. The $(\text{CF}_3)_2\text{PH}$ (mol. wt. 171.8; calcd., 170.0) was measured as a gas. The excess $(\text{CH}_3)_2\text{PH}$ was converted to the slightly volatile hydrochloride and weighed. The dimethylphosphinic acid (m.p. near 91°C ., as known) was freed of dimethylphosphine by vacuum heating and checked by a pH-meter-monitored titration with standard sodium hydroxide, the end-point occurring at $\text{pH} = 6$, in accord with the literature.¹⁰

The Reaction of $\text{P}_2(\text{CF}_3)_4$ with $(\text{CH}_3)_2\text{PH}$. Further evidence of the relative stability of $(\text{CF}_3)_2\text{PH}$ is found in an experiment in which equimolar proportions of $(\text{CH}_3)_2\text{PH}$ and $\text{P}_2(\text{CF}_3)_4$ reacted quantitatively at room temperature to form $(\text{CF}_3)_2\text{PH}$ and the previously-reported (Ref. 4, p. 84) unsymmetrical biphosphine $(\text{CH}_3)_2\text{PP}(\text{CF}_3)_2$. This experiment is summarized as follows:



A second experiment, using a 2:1 ratio of $(\text{CH}_3)_2\text{PH}$ to the biphosphine, showed a slow further reaction which was only 20% complete after 11 days at room temperature. The sense of this reaction seems to have been a displacement of $\text{P}(\text{CF}_3)_2$ groups from $(\text{CH}_3)_2\text{PP}(\text{CF}_3)_2$, to form more $(\text{CF}_3)_2\text{PH}$ and some $\text{P}_2(\text{CH}_3)_4$. The slowness of this reaction might be partly due to a mechanical protection of the biphosphine from the $(\text{CH}_3)_2\text{PH}$ by a layer of the far denser $(\text{CF}_3)_2\text{PH}$.

Attempts to Make Methylated Diphosphoxanes

If it is true that the diphosphoxane $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ and the phosphinous acid $(\text{CF}_3)_2\text{POH}$ owe their existence to the high electronegativity of the CF_3 group, it might be very difficult to make analogous compounds with CH_3 taking the place of CF_3 . The failure of the following highly valid attempts to make the methylated diphosphoxanes would seem to confirm this expectation. The main difficulty probably was a tendency for compounds of the type $\text{R}_2\text{POP}(\text{R})_2$ to convert

to the $\text{R}_2\text{P}-\text{PR}_2$ type, presumably with subsequent disproportionation to biphosphine and a double phosphine oxide. Such a conversion would be like the change of phosphinous esters to tertiary phosphine oxides ($\text{R}_2\text{POR} - \text{R}_3\text{PO}$); but the exact reason for its easier occurrence when R is a hydrocarbon group than when R is a fluorocarbon group can be seen only vaguely in relation to relative electronegativities. So far our negative attempts have involved only $(\text{CH}_3)_2\text{P}$ groups, but it should be most interesting to learn whether CH_3PCF_3 diphosphoxanes and phosphinous acid might be capable of existence.

The Diphosphoxane-Dimethylphosphine Reaction. The existence of the adduct $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2 \cdot (\text{CH}_3)_3\text{N}$ suggested that the same kind of bonding might occur also between the diphosphoxane and $(\text{CH}_3)_2\text{PH}$, namely an attachment of the strongly basic methylated phosphorus to the weakly electron-receptive phosphorus in the diphosphoxane. In that case we would have the first step in a mechanism which would be expected to produce $(\text{CF}_3)_2\text{POH}$ and the unsymmetrical biphosphine $(\text{CH}_3)_2\text{PP}(\text{CF}_3)_2$ (Ref. 4, p. 84). Now this biphosphine is split by either water or HCl to give a 1:1 yield of $(\text{CF}_3)_2\text{PH}$, and we should expect the intermediate-strength acid $(\text{CF}_3)_2\text{POH}$ to attack it in the same manner. The result would be $(\text{CF}_3)_2\text{PH}$ and the desired diphosphoxane $(\text{CH}_3)_2\text{POP}(\text{CF}_3)_2$.

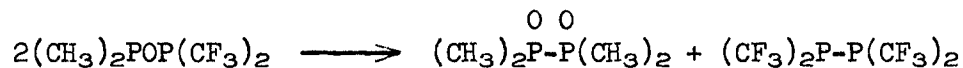
In an exploratory experiment, 0.722 mmole of $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ reacted with 1.03 mmoles of $(\text{CH}_3)_2\text{PH}$, forming 1.005 mmoles of $(\text{CF}_3)_2\text{PH}$ along with a white solid (m.p. 132.5-132.8°C.) and less of a volatile liquid which might have been $(\text{CH}_3)_2\text{POP}(\text{CF}_3)_2$. However, this liquid changed rather quickly (possibly by the effect of mercury, or the white solid, or both), producing some $(\text{CH}_3)_2\text{PP}(\text{CF}_3)_2$. This was identified by its m.p., vapor tensions, and absorption spectra - both ultra-violet (Ref. 4, p. 85) and infra-red.

In the second experiment a nearly equimolar mixture of $(\text{CH}_3)_2\text{PH}$ (0.508 mmole) and $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ (0.512 mmole) was warmed slowly from -60°C. to room temperature, gradually forming a white solid. The volatile products were 90.7 mg. of $(\text{CF}_3)_2\text{PH}$ (0.518 mmole, having mol. wt. 174.8 vs. calcd. 170.0), and an irresolvable mixture of $(\text{CH}_3)_2\text{PP}(\text{CF}_3)_2$ with $\text{P}_2(\text{CF}_3)_4$ (total, 76.6 mg.; ave. mol. wt. near 310; components proved by infra-red spectrum). The residue was the previously-observed white solid (m.p. 132.5-132.7°C.), which could be sublimed under high vacuum at 100°C.

Further Study of the Sublimable White Solid. The white solid product of the $(\text{CH}_3)_2\text{PH}-(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ reaction was studied further in terms of the working

hypothesis that it might be mostly the double phosphine oxide $(\text{CH}_3)_2\text{P}(\text{O})-\text{P}(\text{O})(\text{CH}_3)_2$.

This seemed reasonable in view of the presence of $P_2(CF_3)_4$ among the reaction products, for the full hypothesis would include the disproportionation of the desired diphosphoxane:



The $P_2(CF_3)_4$ naturally would not occur in high yield, since it would be used up by the above-described reaction



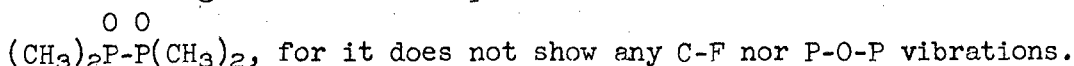
In this white solid the phosphorus atoms evidently were pentavalent, for the substance proved to be inert toward pure oxygen both at room temperature and above its melting point ($133^\circ C.$). Its infra-red spectrum was recorded by the KBr-disc method, giving useful information even though the pattern is fairly complex. For purposes of assignment, the wave-numbers are compared with those for $(CH_3)_3PO$,¹¹ which is quite distinct from the present compound, both in this spectrum and in having a m.p. some seven degrees higher, but has some structural parts in common. The comparison is given by Table XII.

TABLE XII

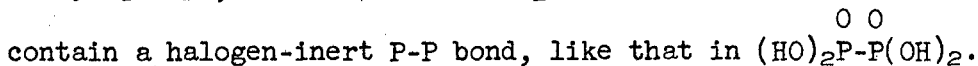
Infra-Red Spectra of the White Solid and $(CH_3)_3PO$

White Solid	$(CH_3)_3PO$	Vibrational Assignments
3030	2923 (Raman)	CH_3 symm. stretch, in phase
1425	1420 1437	CH_3 asymm. bend, out phase
1310	1340 1305 1292	CH_3 symm. bend
1220	1170	P=O stretch
975	950	CH_3 rocking, out phase
910	872	CH_3 rocking, out phase
894	866	CH_3 wag, out phase
760	750	P-C asymm. stretch
705	671 (Raman)	P-C symm. stretch

In view of an actual difference of structure, some of these assignments may not apply very well to the white solid, or at least we must regard the assignments as tentative as far as this compound is concerned. However, it must be recognized that the spectrum is consistent with the structure



An attempt to cleave the postulated P-P bond by chlorine did not succeed, possibly because the conditions were kept mild to avoid chlorination of the methyl groups; thus 99% of the Cl_2 sample was recovered. The compound may



Also negative was an attempt to synthesize a known sample of $(\text{CH}_3)_2\text{P}-\text{P}(\text{CH}_3)_2$ for comparison. Oxygen was allowed to act upon a solution of $\text{P}_2(\text{CH}_3)_4$ in the solvent C_3F_8 . The oxygen-absorption suddenly became slow when the product contained 2.4 oxygen atoms per $\text{P}_2(\text{CH}_3)_4$, but the product was a non-volatile viscous oil rather than the expected white solid. Aside from the probable formation of peroxides, the reaction was complex enough to produce traces of CH_3PH_2 and $(\text{CH}_3)_2\text{PH}$. Further work on the synthesis of this double phosphine oxide is planned, as well as studies to elucidate the over-all process of the reaction of $(\text{CH}_3)_2\text{PH}$ with $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$.

The Reaction of $(\text{CF}_3)_2\text{POH}$ with $(\text{CH}_3)_2\text{PP}(\text{CF}_3)_2$. If the first stage of the reaction of $(\text{CH}_3)_2\text{PH}$ with $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ really is the formation of $(\text{CF}_3)_2\text{POH}$ and $(\text{CH}_3)_2\text{PP}(\text{CF}_3)_2$, the further reaction of these products is worthy of direct study. A reasonable possibility would be their conversion to $(\text{CF}_3)_2\text{PH}$ and the unsymmetrical diphosphoxane $(\text{CH}_3)_2\text{POP}(\text{CF}_3)_2$, which might well disproportionate to $\text{P}_2(\text{CF}_3)_4$ and $(\text{CH}_3)_2\text{P}-\text{P}(\text{CH}_3)_2$.

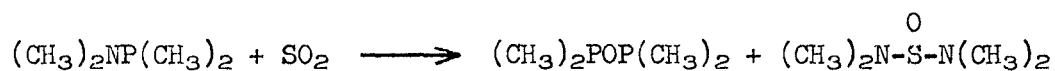
In order to test this hypothesis, a mixture of 0.108 mmole of $(\text{CH}_3)_2\text{PP}(\text{CF}_3)_2$ and 0.108 mmole of $(\text{CF}_3)_2\text{POH}$ (measured by gas volume and so possibly underestimated) were held together at room temperature for 16 hours. There was a gradual formation of a white solid which melted at $132.5-132.7^\circ\text{C}$. - evidently the same as that obtained from the $(\text{CH}_3)_2\text{PH}-(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ reaction. From the volatile product it was possible to isolate 0.111 mmole of pure $(\text{CF}_3)_2\text{PH}$ (6.3 mm. at -78.5° , as calcd.; mol. wt. 171.8 vs. calcd. 170.0), corresponding to the postulated reaction



A mixed fraction, less volatile than $(\text{CF}_3)_2\text{PH}$ and amounting to 0.1 mmole, was not identified.

Attempts to Make Tetramethyldiphosphoxane. Attempts to synthesize $(\text{CH}_3)_2\text{POP}(\text{CH}_3)_2$ by a method which succeeded in the case of $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ - in this case the reaction between Ag_2CO_3 and $(\text{CH}_3)_2\text{PCl}$ - were wholly unsuccessful. A reaction occurred readily enough but no volatile material could be recovered. If any $(\text{CH}_3)_2\text{POP}(\text{CH}_3)_2$ had formed, it should not have been appreciably less volatile than $\text{P}_2(\text{CH}_3)_4$, which is easily distillable in the high-vacuum system. However, its rearrangement into a phosphine-oxide form, and possibly other reactions afterwards, could be expected.

Another approach was based upon the hope that the reaction



could be made to occur, especially since the second product is a known stable compound. However, no such reaction occurred even at 100°C. On cooling, it was possible to demonstrate the adduct $(\text{CH}_3)_2\text{NP}(\text{CH}_3)_2 \cdot 1.5\text{SO}_2$, which went to the 0.5SO_2 adduct under vacuum at room temperature.

Yet another attempt was based upon the reaction of $(\text{C}_2\text{H}_5)_2\text{PH}$ with $(\text{CH}_3)_2\text{POCl}$.

In this case one might have expected to form a phosphine oxide of the type $\text{R}_2\text{P}(\text{O})\text{PR}_2$, but the chance of a POP form could not be eliminated. The actual reaction led only to unidentifiable non-volatile products.

CHAPTER IV

TRIFLUOROMETHYL-BROMO-PHOSPHINES AND PHOSPHORANES

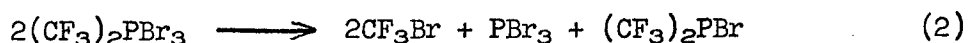
The cleavage of the P-CF₃ bond by halogens has been known for some time; for example the biphosphine P₂(CF₃)₄ heated with excess iodine or bromine eventually yields all of the CF₃ groups as CF₃I or CF₃Br, or (CF₃)₃P with I₂ gives CF₃I, (CF₃)₂PI, CF₃PI₂ and PI₃.¹² These reactions are interesting to the present project on account of their relation to the process whereby we obtain our (CF₃)₂P- and CF₃P= compounds. It has been a matter of some curiosity that the end result is replacement of the highly electronegative CF₃ group by presumably less electronegative bromine or iodine. The manner in which this happens has not been understood, for the reactions have been carried out only at relatively high temperatures, so that nothing could be learned of the intermediate stages.

Our initial studies of the P₂(CF₃)₄-Br₂ reaction indicated the formation of the phosphorane (CF₃)₂PBr₃ and suggested that the loss of CF₃Br from this and other phosphoranes might be the chief mechanism for removing the highly electronegative CF₃ group from its bond to phosphorus. This bromine reaction seemed best for further study, since iodophosphoranes cannot be prepared at convenient temperatures, if at all, and chlorophosphoranes tend to be either too stable - e.g. CF₃PCl₄-¹³ or explosive under certain conditions - e.g. (CF₃)₃PCl₂.¹² However, the intermediate bromophosphoranes proved to be both recognizable and subject to decomposition under mild conditions.

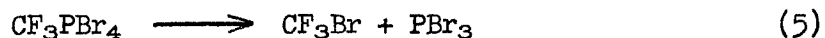
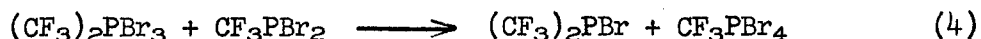
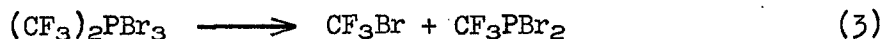
The first step of the action of bromine upon P₂(CF₃)₄ is the virtually quantitative P-P bond cleavage



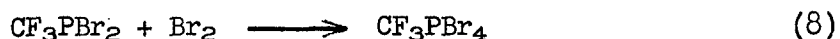
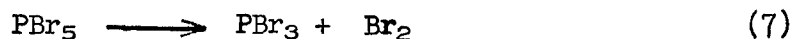
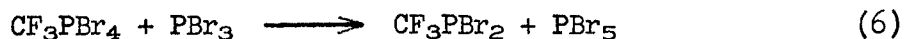
This is followed by the almost quantitative conversion of the (CF₃)₂PBr to the phosphorane (CF₃)₂PBr₃ (m.p. 6.0-9.4°C.), which cannot be characterized quite satisfactorily on account of the slow decomposition



A reasonable hypothesis concerning this decomposition, to account for the various experimental observations as well as the over-all stoichiometry, would be the following set of component processes



complicated by

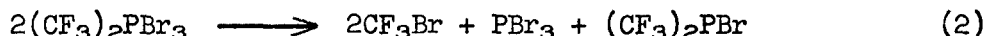
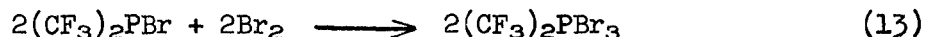
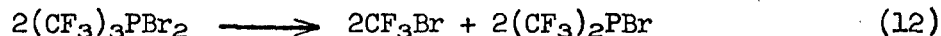
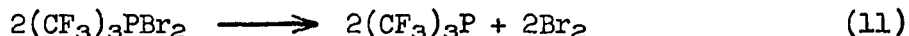
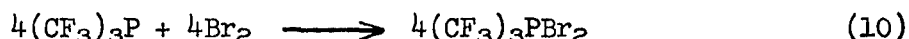


Reactions (5), (6) and (8) were verified by individual experiments. The completion of reaction (7) above 65° has been demonstrated elsewhere.¹⁴ Reactions (3) and (4) could not be separated; when (3) was tried, it supplied CF₃PBr₂ for the similarly rapid reaction (4); and when (4) was tried, the stoichiometry could be balanced only by assuming some occurrence of (3). It seems highly probable that (3) is the first step in the over-all process (2); the alternative disproportionation



is not a probable part of the process, for (CF₃)₃PBr₂ decomposes more easily than (CF₃)₂PBr₃, and would have produced (CF₃)₃P, which could not be found among the products. Certainly process (2) is well represented by the sum of reactions (3), (4) and (5); and it seems that the complicating effect of (6) (which we have found to be complete in 30 min. at 35°) is overcome by (7), occurring appreciably only at higher temperatures.¹⁴

The foregoing discussion suggests also a reasonable scheme of reactions whereby a halogen acts upon (CF₃)₃P to form (CF₃)₂PX and CF₃PX₂ compounds. In particular, the action of bromine on tris(trifluoromethyl)phosphine can be represented by the sequence



Thus some of the (CF₃)₃P would be regained by reaction (11), which would supply bromine for reaction (13). The formation of CF₃PBr₂ can be ascribed to reaction (3). The elimination of CF₃Br from (CF₃)₃PBr₂ (equation 12) was not proved directly, but it seems more probable than the disproportionation of (CF₃)₃PBr₂, in the light of arguments already presented.

It is interesting that reactions (4) and (6) and the sum of (11) and (13) all imply that the trifluoromethyl bromo phosphoranes are stabler with more Br and less CF₃. Evidently the P-Br bond in (CF₃)_nPBr_{5-n} becomes weaker with increasing n. In fact, reaction (10) could be recognized only by the complete fading out of the bromine color, whereas the more brominated phosphoranes could be obtained as more distinctly recognizable compounds.

A primary reason for the weakening of P-Br bonding by CF₃ groups probably is steric interference; more subtle effects such as different hybridization for maximum overlap in P-CF₃ vs. P-Br bonds, or the induction of greater electronegativity for P, so that the P-Br bonds become less polar, are difficult to evaluate.

The above discussion is supported by the following experimental details

Apparatus, Techniques, and Materials

Various experiments involving mercury-reactive substances were performed in a mercury-free high-vacuum manifold, with the stop-cocks lubricated by a halo-carbon grease supplied by Halocarbon Products Corporation, Hackensack, New Jersey. When mercury manometers could not be used directly, pressure measurements were done by means of a null-indicating Pyrex-glass sickle gauge,¹⁵ placed with the pointer vertically upward so that the sample could be completely immersed in a constant-temperature bath for vapor tensions above room temperature. Above -25° , temperatures were measured by mercury-in-glass thermometers; and for lower temperatures the appropriate vapor-tension thermometers¹⁶ were employed.

Infra-red absorption spectra were recorded by means of a Perkin-Elmer Infra-cord instrument with sodium-chloride optics, using a gas-cell 71 mm. long and having potassium-bromide windows fastened by Apiezon W wax.

Bromine was purified by repeated contact with P_4O_{10} and high-vacuum distillation through one trap at -45° to another at -78° . The CF_3 -P-I phosphines were made by known methods,^{12,17} as was also the biphosphine $P_2(CF_3)_4$.¹² This showed 22.0 mm. pressure as found earlier (Ref. 1, p. 33).

The Compound Bis(trifluoromethyl)bromophosphine

Synthesis.-- A mixture of 0.306 mmole of $P_2(CF_3)_4$ with 0.227 mmole of Br_2 reacted at room temperature, with immediate fading of the bromine color. For certain completion of the reaction, the mixture was heated for 40 hr. in a sealed tube at 90° , and then resolved by high-vacuum fractional condensation. The resulting 0.435 mmole of $(CF_3)_2PBr$ (mol. wt. 249.8; calcd., 248.9) represented 96% of the Br_2 . It condensed out at -105° , having passed a trap at -78° , which retained the unused $P_2(CF_3)_4$ (21.9 mm. at 0° ; 0.072 mmole of calcd. 0.079). The only other component was 0.016 mmole of CF_3Br (mol. wt. 145; calcd., 148.6).

If a large excess of bromine is used for reaction with $P_2(CF_3)_4$, all CF_3 groups are removed at temperatures as low as 90° . The experiment was not tried directly, but the conclusion can be argued from the above synthesis and reactions (2) and (13). With a $Br_2:P_2(CF_3)_4$ ratio between 2 and 1, the products are more various, as described later.

An alternative synthesis was by the reaction of $(CF_3)_2PI$ with silver bromide, 10 g. of which was kept in a sealed tube with 11.28 mmoles of $(CF_3)_2PI$ (44.0 mm. at 0° , in accord with the known value)¹⁷ for 96 hr. The yield of $(CF_3)_2PBr$ was 11.03 mmoles, or 97.8%. However, it was not possible to remove a trace of unused $(CF_3)_2PI$, which was detectable by its action upon mercury. The pure sample of $(CF_3)_2PBr$, made by the cleavage of $P_2(CF_3)_4$, proved to be inert toward mercury at 25° and showed 140.0 mm. pressure at 0° . The sample from the $AgBr-(CF_3)_2PI$ reaction showed 132.3 mm. pressure at 0° .

Confirmation of the Formula.-- Alkaline hydrolysis of 100.7 mg. of the product gave 0.811 mmole of HCF_3 (calcd., 0.810; mol. wt. 70.0, as calcd; vapor tension 93.5 mm. at -111.6° vs. calcd. 94.0 mm.). The gas-phase mol wt. was determined as 248.9, exactly as calcd. for $(CF_3)_2PBr$.

Volatility.-- The tensiometrically uniform product from the bromine-cleavage of $P_2(CF_3)_4$ had the vapor-tension values shown in Table XIII. These determined

the equation $\log p_{\text{mm}} = 5.8940 - 0.00566T + 1.75 \log T - 1766.5/T$, giving the normal b.p. as 42.2° and the Trouton constant as 21.0 cal./deg.mole. The m.p. could not be observed because the material formed a glass at low temperatures.

TABLE XIII

Vapor Tensions of Liquid $(\text{CF}_3)_2\text{PBr}$

t ($^\circ\text{C.}$)	p_{mm} (obsd.)	p_{mm} (calcd.)	t	p (obsd.)	p (calcd.)
-45.6	9.86	9.89	0.0	140.0	140.0
-31.0	25.23	25.23	7.9	200.9	201.6
-23.2	39.7	40.6	14.8	270.9	271.7
-10.3	84.5	83.5	23.4	382.2	382.2

The Compound Trifluoromethyl-dibromophosphine

Synthesis.-- A 4.92 mmole sample of CF_3PI_2 (slightly contaminated with iodine) was shaken periodically with silver bromide (8.0 g.) in a sealed tube at room temperature, during one week. The product was subjected to high-vacuum fractional condensation, passing a trap at -35° and condensing at -78° . The yield was 4.55 mmoles (92.5%).

Confirmation of Formula.-- The mol. wt. of the product was determined in the vapor phase, as 260.0 (calcd., 259.8). The alkaline hydrolysis of an 89.1 mg. sample gave 0.347 mmole of authenticated HCF_3 (calcd., 0.343 mmole). The infra-red spectrum (see Table III) corresponded to expectations for CF_3PBr_2 .

Volatility.-- The vapor tensions of a tensiometrically uniform sample of CF_3PBr_2 were obtained by means of the sickle gauge. The results, shown in Table XIV, determined the equation $\log p_{\text{mm}} = 3.8579 - 0.00206T + 1.75 \log T - 1694.74/T$, according to which the normal b.p. would be 86.7° and the Trouton constant 21.7 cal./deg.mole

TABLE XIV

Vapor Tensions of Liquid CF_3PBr_2

t ($^\circ\text{C.}$)	p_{mm} (obsd.)	p_{mm} (calcd.)	t	p (obsd.)	p (calcd.)
-23.2	5.8	5.8	14.2	47.2	46.8
-9.7	12.9	13.1	22.8	70.2	70.3
0.0	22.6	22.6	30.4	98.5	98.5
6.7	32.3	32.2	37.3	131.5	131.9

This substance also formed a glass at low temperatures, so that the m.p. could not be observed.

Infra-Red Spectra

The infra-red spectra of $(\text{CF}_3)_2\text{PBr}$ and CF_3PBr_2 in the sodium-chloride region are summarized in Table XV. They are similar to those of other $\text{CF}_3\text{-P}$ halides of P(III), conforming to the general observation that the frequencies of C-F stretching vibrations in $\text{CF}_3\text{-P}$ compounds are split into $n + 1$ bands, where n is the number of CF_3 groups on each phosphorus atom.^{12,13}

TABLE XV

Vibration Frequencies of $(\text{CF}_3)_2\text{PBr}$ and CF_3PBr_2

$(\text{CF}_3)_2\text{PBr}$		CF_3PBr_2	
Frequency (cm. ⁻¹)	Assignment	Frequency (cm. ⁻¹)	Assignment
2275 w.	2 x 1145	2265 vs.	2 x 1135
1425 vw. } 1315 s. } 1282 s. }	Overtones or Combinations	1410 vw. } 1300 m. } 1270 w. }	Overtones or Combinations
1220 vs. } 1177 vs. } 1145 vs. }	C-F Stretching	1190 vs. } 1135 vs. }	C-F Stretching
755 s. } 728 vw. }	C-F Bending	745 s.	C-F Bending

The Trifluoromethyl-Bromo-Phosphoranes

The Tribromophosphorane; Reaction (2).-- An equimolar mixture (1.03 mmoles each) of $(\text{CF}_3)_2\text{PBr}$ and Br_2 was warmed to room temperature, with immediate fading of the bromine color. The product was subjected to high-vacuum fractional condensation at -55° (removing 0.08 mmole of CF_3Br) and then appeared as a white solid melting to a pale yellow liquid in the range $6.0\text{-}9.4^\circ$. It was not appreciably volatile at 0° . A 0.414 mmole sample of this product, presumed to be $(\text{CF}_3)_2\text{PBr}_3$, decomposed slowly at room temperature and completely at 90° , with transient appearance of two solids. The first of these had the m.p. (28°) and bright orange color of CF_3PBr_4 . The second, having the lemon-yellow color of PBr_5 (per reaction 6) disappeared with rising temperature, to form a bromine-like vapor.

After the decomposition was complete (as judged by the absence of color) high-vacuum fractional condensation was used to isolate and purify the products, which could be identified by their molecular weights. The yields and molecular weights are shown in relation to equation (2) as follows.

	$2(\text{CF}_3)_2\text{PBr}_3$	\longrightarrow	$2\text{CF}_3\text{Br}$	$+$	PBr_3	$+$	$(\text{CF}_3)_2\text{PBr}$
Amount (mmoles)	0.414		0.412		0.188		0.210
Mol. wt. obsd.	-		148.7		271.7		252.5
calcd.	-		148.9		270.7		248.9

The 9% deficiency in the yield of PBr_3 is attributed to its tendency to dissolve in the halocarbon stop-cock grease - an effect which could not be entirely overcome. For further identification its vapor tension was measured as 4.0 mm. at 29° (calcd. from literature equations, 3.9 mm.).

The Tetrabromophosphorane; Reaction (5).-- A bright-orange-colored solid, melting almost completely in the range 28.3 - 28.5° , was formed from 0.537 mmole of CF_3PBr_2 and 0.406 mmole of Br_2 , slowly warmed together from -196° . No free Br_2 could be recovered by distillation at -64° but it was possible to isolate 0.075 mmole of CF_3Br and 0.128 mmole of CF_3PBr_2 (mol. wt. 258.8; calcd., 259.8), leaving a product having the composition of 0.40 mmole of CF_3PBr_4 . On heating for 30 min. at 90° , the sample became colorless; and after 16 hr. at that temperature, the products were separated and measured. The over-all process (corrected for the initial excess of CF_3PBr_2) is expressed by the following equation, with quantities and evidences of identity.

	CF_3PBr_2	$+$	Br_2	\longrightarrow	CF_3PBr_4	\longrightarrow	CF_3Br	$+$	PBr_3
Amount (mmoles)	0.402		0.405		(orange)		0.404		0.403
Mol. wt. obsd.	260.7		159.3				147.6		-
calcd.	259.8		159.8				148.6		-
m.p.	obsd.	-	-				-		-39.2°
	known	-	-				-		-40.0°

Evidence of Reactions (3) and (4).-- The reaction between $(\text{CF}_3)_2\text{PBr}_3$ and CF_3PBr_2 was most reasonably explained in terms of equations (3) and (4), neither of which could be separately verified to the exclusion of the other. A sample of $(\text{CF}_3)_2\text{PBr}_3$ was made from 0.312 mmole each of $(\text{CF}_3)_2\text{PBr}$ and Br_2 at room temperature, and treated with 0.311 mmole of CF_3PBr_2 . After 66 hr. at 27° the yield of CF_3Br (0.05 mmole) indicated only 16% completion of the reaction, but a 12-hr. heating in a sealed tube at 95° brought the process to completion, as shown by the following tabulation of products and evidences of identity.

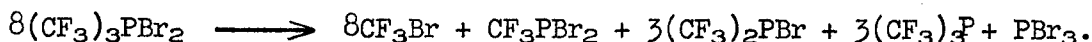
Compound	CF_3Br	$(\text{CF}_3)_2\text{PBr}$	CF_3PBr_2	PBr_3
Mmoles obsd.	0.307	0.206	0.208	0.140
Mmoles calcd.	0.312	0.206	0.211	0.206
Mol. wt. obsd.	-	248.9	261.4	-
Mol. wt. calcd.	-	248.9	259.8	-

Volatility of CF_3Br : 251.8 mm. at -78.5 (calcd. 252.0 mm.);
volatility of PBr_3 judged qualitatively.

The calculated quantities here are based upon the assumption that 0.106 mmole of $(\text{CF}_3)_2\text{PBr}_3$ went to form CF_3Br and CF_3PBr_2 (equation 3), so that the use of the remaining 0.206 mmole of $(\text{CF}_3)_2\text{PBr}_3$ for the transfer of Br_2 to CF_3PBr_2 (equation 4) required only 0.100 mmole of the 0.311 mmole initial sample of CF_3PBr_2 . The low yield of PBr_3 again is to be ascribed to the condition of the stop-cocks; with time there is an increase in the amount of grease squeezed out into the space available to the vapors; and a trace of bromine in the grease makes it especially effective for absorbing PBr_3 .

The Bromine-Transfer Reaction (6).-- A 0.242 mmole sample of CF_3PBr_4 was made by mixing equimolar portions of CF_3PBr_2 and Br_2 , which reacted completely within a few minutes at 0° . Then 0.311 mmole of PBr_3 (m.p. -39.2 ; reported value, -40.0°) was added and the mixture was heated for 30 min. at 35° . Now it was possible to isolate 0.03 mmole of CF_3Br and 0.212 mmole of CF_3PBr_2 (volatility 22.8 mm. at 0° ; known, 22.6 mm.). The remaining mixture weighed 118.2 mg.; calcd. as $\text{PBr}_3 + \text{PBr}_5$, 118.7 mg. The PBr_5 appeared as a lemon-yellow solid even at 45° , and could be sublimed in vacuo at room temperature, along with the distilling PBr_3 .

Tris(trifluoromethyl)phosphine with Bromine.-- Equimolar samples of $(\text{CF}_3)_3\text{P}$ and Br_2 were brought together by condensation at -196° and warmed to room temperature. The initially immiscible liquids reacted slowly to form a single colorless liquid, having the composition of the formula $(\text{CF}_3)_3\text{PBr}_2$. In the initial experiment this product was heated for 18 hr. at 80° , with results roughly summarized by the over-all empirical equation

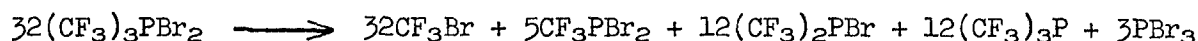


This experiment was regarded as tentative because the fraction representing the $(\text{CF}_3)_2\text{PBr}$ and $(\text{CF}_3)_3\text{P}$ was not fully resolved; however the weight of this fraction, taken with the accurately observed yields of CF_3Br and CF_3PBr_2 , required this equation for a correct material balance.

A considerably more accurate experiment began with 1.008 mmole of $(\text{CF}_3)_3\text{P}$ and 1.005 mmole of Br_2 . A 9-hr. heating at 90° yielded a mixture which was resolved by high-vacuum fractional condensation, into the following four fractions.

- (a) CF_3Br , 150.0 mg. (1.007 mmoles); mol. wt. 148.8 (calcd. 148.9); 252.3 mm. at -78.5° (calcd., 252.0 mm.).
- (b) $\text{CF}_3\text{PBr}_2 + \text{PBr}_3$, 43.7 mg. (0.165 mmole by rough volume msmt.). This was hydrolyzed in 15% NaOH (30 hr. at 100°) to give 11.1 mg. of HCF_3 (0.159 mmole; mol. wt. 69.8 vs. calcd. 70.0); then a Volhard determination of bromide in acid solution showed 0.338 meq. Hence the fraction seemed to consist of 0.159 mmole of CF_3PBr_2 with 0.007 mmole of PBr_3 .
- (c) $(\text{CF}_3)_2\text{PBr} + (\text{CF}_3)_3\text{P}$, 180.5 mg. (0.749 mmole by volume). An analysis as in (b) gave 1.752 mmoles of HCF_3 and 0.320 meq. of Br^- ; however these results would imply only 0.371 mmole of $(\text{CF}_3)_3\text{P}$ and 0.320 mmole of $(\text{CF}_3)_2\text{PBr}$, falling short of the observed 0.749 mmole for the two together.
- (d) PBr_3 , 26.8 mg. (0.099 mmole by volume); mol. wt. 271 (calcd. 270.7); 2.7 mm. at 23.5° (calcd. 2.7).

This analysis is summarized by the over-all empirical equation



Mmoles calcd.	1.005	1.005	0.157	0.377	0.377	0.094
Mmoles obsd.	1.005	1.007	0.159	0.749		0.106

Although much of this process may have gone according to equation (12), processes (11), (13) and (2) also would account for the equimolar yield of CF_3Br , and seem necessary to explain the formation of $(\text{CF}_3)_3\text{P}$, CF_3PBr_2 , and PBr_3 . The alternative idea that these formed by disproportionation of $(\text{CF}_3)_2\text{PBr}$ seems to require that CF_3Br be reabsorbed by $(\text{CF}_3)_2\text{PBr}$ to form $(\text{CF}_3)_3\text{PBr}_2$. Such a step would contradict the whole trend of individually observed reactions favoring the more highly brominated phosphoranes.

Miscellaneous Trifluoromethyl-Phosphorus Halide Chemistry

Bis(trifluoromethyl)bromophosphine and Mercury.-- Although $(\text{CF}_3)_2\text{PBr}$ seems to be quite inert toward mercury at room temperature, a 0.321 mmole sample, heated with mercury for 16 hr. at 100° (without shaking) was 80% converted to $\text{P}_2(\text{CF}_3)_4$ (0.128 mmole), with recovery of 0.067 mmole of the original $(\text{CF}_3)_2\text{PBr}$.

The Tribromophosphorane with Mercury.-- The existence of $(\text{CF}_3)_2\text{PBr}_3$ made possible an experiment to determine whether the room-temperature inertness of $(\text{CF}_3)_2\text{PBr}$ toward mercury would persist even when this bromophosphine is being formed by a chemical reaction. A 144.3 mg. sample of $(\text{CF}_3)_2\text{PBr}_3$ (only slightly contaminated by the decomposition products CF_3PBr_4 and PBr_3) reacted rapidly with mercury in a sealed tube at room temperature. After some shaking, the mixture yielded 0.321 mmole of $(\text{CF}_3)_2\text{PBr}$ (calcd., 0.354 mmole; mol. wt. 248.6 vs. calcd. 248.9) as the only volatile product. Thus 91% of the expected $(\text{CF}_3)_2\text{PBr}$ withstood the action of mercury during formation.

Trifluoromethyl-dibromophosphine with Mercury.-- Unlike $(\text{CF}_3)_2\text{PBr}$, the dibromophosphine CF_3PBr_2 reacts easily with mercury, to form CF_3P -polymers at room temperature. A 66.2 mg. sample of CF_3PBr_2 (0.255 mmole) was shaken briefly with excess mercury and the products separated. The main component was the equilibrium mixture of $(\text{CF}_3\text{P})_4$ and $(\text{CF}_3\text{P})_5$,¹³ altogether amounting to 15.7 mg., and representing 70% of the CF_3PBr_2 . The recovery of this dibromophosphine was 11.0 mg. (17%). The remaining CF_3P units (13%) presumably were aggregated as involatile higher polymers.

Synthesis of $(\text{CF}_3\text{P})_{4,5}$ by Use of Antimony. The need for a new supply of $(\text{CF}_3\text{P})_4$ and $(\text{CF}_3\text{P})_5$ provided the opportunity to try CF_3PI_2 with antimony instead of mercury, and this method of removing the iodine proved to be more convenient as well as less expensive. The antimony method has the advantage that the metal iodide is fairly low-melting, so that the reaction at 100° can be done mostly with a liquid phase in contact with fresh metal, and no shaking is required. Two experiments, each employing about 2 mmoles of CF_3PI_2 and 1 g. of powdered antimony, in sealed tubes for 12 hours at 100°C ., gave nearly quantitative yields of the usual tetramer-pentamer mixture.

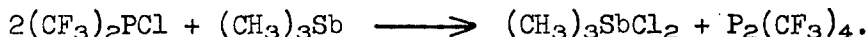
Reaction of the Dibromide with Antimony. Having proved effective for converting CF_3PI_2 to the CF_3P tetramer and pentamer, powdered antimony was tried with CF_3PBr_2 for the same purpose. The 4.5 g. sample of Sb completely consumed the 0.723 mmole of CF_3PBr_2 during 60 hours in a sealed tube at 100°C ., but there was scarcely any volatile product except a 9.8% yield of the CF_3P tetramer-pentamer mixture. Possibly the antimony had some specific effect upon the dibromide - unlike its reaction with CF_3PI_2 — such that most of the CF_3P groups formed higher polymers; but this is not yet known.

Trimethylstibine as a Dechlorinator. Both $(\text{CF}_3)_2\text{PCl}$ and CF_3PCl_2 transfer chloride to $(\text{CH}_3)_3\text{Sb}$ to make $(\text{CH}_3)_3\text{SbCl}_2$ and the corresponding P-P compounds. Thus 2.34 mmoles of CF_3PCl_2 and 1.637 mmoles of $(\text{CH}_3)_3\text{Sb}$ reacted rapidly at room temperature to form 143.2 mg. of CF_3P tetramer and pentamer mixture, having the typical average molecular weight (417) of the equilibrium mixture. The recovery of CF_3PCl_2 amounted to 0.721 mmole, meaning that 1.62 mmoles of it had reacted with nearly the same molar quantity of $(\text{CH}_3)_3\text{Sb}$, according to the equation



However, the yield of the CF_3P tetramer and pentamer was only 88%, suggesting that some higher CF_3P polymer might have formed in the rapid and somewhat random reaction.

Similarly, but somewhat more slowly, 1.67 mmoles of $(\text{CF}_3)_2\text{PCl}$ and 0.773 mmole of $(\text{CH}_3)_3\text{Sb}$ reacted somewhat incompletely during two days at room temperature, and were allowed a third day for completion of the process. Now 0.20 mmole of $(\text{CF}_3)_2\text{PCl}$ could be recovered, and the yield of $\text{P}_2(\text{CF}_3)_4$ (M.W. 339.5 vs. calcd. 338; v.t. 22 mm. at 0°C .) was 219.3 mg. (0.648 mmole), or 88% in terms of the equation



Some 16% of the trimethylstibine apparently had reacted otherwise, for it was not present as an appreciable contaminant in the biphosphine, from which it would have been difficult to separate. There was a yellow liquid by-product which might indicate some kind of combination of $(\text{CH}_3)_3\text{Sb}$ with $\text{P}_2(\text{CF}_3)_4$, possibly in the manner of the $(\text{CH}_3)_3\text{P}-\text{P}_2(\text{CF}_3)_4$ combination.

These methods of getting the biphosphine and the CF_3P ring polymers represent an interesting departure from the relatively tedious processes requiring mercury, although trimethylstibine cannot be called a cheap and available reagent. However, it can be recovered for re-use if desired, by shaking the dichloride with zinc dust. It still would be useful to find a more easily available dehalogenating agent, and accordingly sulfur dioxide was tried with CF_3PCl_2 and with CF_3PI_2 at room temperature, and phosphorus trichloride with CF_3PCl_2 at room temperature and at 100°C . All of these mixtures were inert. White phosphorus failed to reduce CF_3PCl_2 alone or in refluxing benzene.

Conversion of $(\text{CF}_3)_2\text{PCl}$ to $(\text{CF}_3)_2\text{PI}$. Some of our syntheses involving $(\text{CF}_3)_2\text{PI}$ have required conversion of the unused iodide to the chloride $(\text{CF}_3)_2\text{PCl}$ to permit purification of the product, and a number of others have produced $(\text{CF}_3)_2\text{PCl}$ more directly. This chloride is so much less useful for most of our purposes, that we

have explored its reconversion to the iodide. The ammonolysis of the chloride gave only a 55% yield of the amide $(\text{CF}_3)_2\text{PNH}_2$, which reacted with HI to give in turn a 54% yield $(\text{CF}_3)_2\text{PI}$. These results probably can be improved by using dimethylamine instead of ammonia.

The Phosphine Method of Making CF_3PH_2 . The G. S. Harris method of reducing $(\text{CF}_3)_2\text{PI}$ to $(\text{CF}_3)_2\text{PH}$ by the action of PH_3 ¹⁸ has been applied to the synthesis of CF_3PH_2 . In contrast to the relatively slow Harris reaction, CF_3PI_2 as a liquid reacted instantaneously with gaseous PH_3 , well below room temperature. The yield of CF_3PH_2 was 91%, at the expense of 2.14 PH_3 per original CF_3PI_2 . A white sublimable by-product was recognized as PH_4I , and there was an orange-colored non-volatile solid. The CF_3PH_2 was identified by its molecular weight (101.8; calcd. 102.0) and vapor tension at -78.5°C . (44 mm. vs. literature 45).

CHAPTER V

CHEMICAL CONSEQUENCES OF THE CF_3P GROUP

The free CF_3P group has a potentially large chemistry, for its two lone pairs of electrons are available for bonding to acceptor groups, while the empty bonding orbital is capable of bonding phosphorus to electron-donor groups. Thus if it were incorporated in a polymer chain of some kind, such as one made of the $(\text{--CF}_3\text{P--C}_2\text{H}_4\text{--})$ unit, there still would be a lone pair of electrons on phosphorus, which thus would have considerable base-strength to offer for cross links with acceptors (such as boron) in other parts of the polymer. This is only one example of a considerable number of possible uses of the CF_3P unit as a connecting link, and accordingly it becomes useful to learn enough of its chemistry to make it applicable.

One very promising approach toward a controlled use of the CF_3P group is offered by the existence of the unstable monomer-complex $(\text{CH}_3)_3\text{PPCF}_3$ (Ref. 4, p. 95). At the time of its discovery, this was shown to lose $(\text{CH}_3)_3\text{P}$ in vacuo, to give the 83:17 equilibrium mixture of $(\text{CF}_3\text{P})_4$ and $(\text{CF}_3\text{P})_5$. However, a sudden chemical removal of $(\text{CH}_3)_3\text{P}$ might lead through a more random process to higher CF_3P polymers; or a slow chemical removal of the $(\text{CH}_3)_3\text{P}$ might permit the formation of CF_3P -chain complexes of the $(\text{CH}_3)_3\text{P}(\text{CF}_3\text{P})_n$ type, fragments from which could react with the phosphine-removing reagent to make stable chain compounds. All of these different types of reaction seem to have been illustrated in our exploratory experiments on the action of HCl or CH_3Cl on $(\text{CH}_3)_3\text{PPCF}_3$. However, it is difficult to draw secure conclusions on the character of these reactions because more work will be required to be sure of the character of the products. Our study of the reaction of $(\text{CH}_3)_3\text{PPCF}_3$ with CH_3I has been more thorough, leading to a product which seems to be mostly the salt $(\text{CH}_3)_3\text{PPCH}_2\text{CF}_3^+\text{I}^-$. This reacts with HCl to give a fairly good yield of $\text{CH}_3\text{CF}_3\text{PX}$ ($\text{X} = \text{Cl}$ or I), from which it is easy to make the new aminophosphine $(\text{CH}_3)_2\text{NPCH}_2\text{CF}_3$ and from that a pure sample of the new chlorophosphine $\text{CH}_3\text{CF}_3\text{PCL}$. From these it is possible to approach the corresponding phosphine biphosphine, and phosphinoborine polymer; and a start toward these has been made by the reaction of diborane with the aminophosphine, with results not yet complete. The biphosphine is regarded as especially important because it could be used not only for making the phosphinoborine polymers, but also for addition to alkenes and alkynes to make new double-tertiary phosphines having promise for inclusion in boron-hydride resins.

Exploratory Experiments with the Monomer Complex

Procedure for Synthesis. For each of the experiments here described, the complex $(\text{CH}_3)_3\text{PPCF}_3$ was made almost quantitatively by exposing a $(\text{CF}_3\text{P})_n$ ring compound to a measured excess of $(\text{CH}_3)_3\text{P}$ in a bomb tube attached to the high-vacuum system through a mercury float-valve. After standing at least 8 hours at room temperature, the material was freed of the excess $(\text{CH}_3)_3\text{P}$ by a two-hour high-vacuum distillation at -70°C . Measurement of the $(\text{CH}_3)_3\text{P}$ before and after the reaction showed the product to have very nearly one $(\text{CH}_3)_3\text{P}$ per CF_3P unit.

The HCl Reaction. A 1.16 mmole sample of the complex was treated with 4.23 mmoles of HCl , with the sealed-off bomb-tube inverted and shaken for maximum contact of reactants, at $55\text{--}60^\circ\text{C}$. After 15 minutes the tube was opened to the high-vacuum system and the volatile components resolved by high-vacuum fractional condensation methods. The yields of the fractions corresponding to CF_3PH_2 and

CF_3PCl_2 were very close to 16%, but they were so difficult to purify as to suggest the presence of an intermediate such as CF_3PHCl . The recovery of the CF_3P tetramer and pentamer was slight, suggesting that the rapid liberation of the unit in high concentration had led to formation of the high polymer as a component of the non-volatile solid. However, this is still to be checked, as by re-formation of the monomer complex. There was no more than the slightest indication of any dimer or trimer of the CF_3P unit. If there were no unexpected complications, it would seem that the conversion to the $(\text{CF}_3\text{P})_x$ high polymer might have been as high as 67%.

The Reaction with Methyl Chloride. Methyl chloride was chosen for a slow reaction with the complex $(\text{CH}_3)_3\text{PPCF}_3$, because the strength of the C-Cl bond makes it fairly slow to attach to trimethylphosphine and so allows the possibility of different reactions at preferential rates under some control. Preliminary experiments showed no reaction between CH_3Cl and $(\text{CH}_3)_3\text{P}$ in the vapor phase during 12 hours at room temperature, and only 10% of the expected formation of $(\text{CH}_3)_4\text{PCl}$ occurred during 90 minutes at 100°C . In the liquid phase, there seemed to be some slight reaction during some hours of warming from -78 to -46°C ., and after 22 hours at 0°C . the addition was 85% complete. Thus it seemed that $(\text{CH}_3)_3\text{P}$ would not be removed at all rapidly from the complex $(\text{CH}_3)_3\text{PPCF}_3$ and that the PCF_3 groups would become available at very low concentrations. The results of the attack of this complex by CH_3Cl indicated that these PCF_3 units tended to form chains rather than pick up CH_3Cl directly, for the absorption of CH_3Cl was considerably less than would correspond to 1:1 attachment both to PCF_3 units and to trimethylphosphine. The PCF_3 -chain formation was indicated by the presence of at least two products propoing to be methylated polyphosphines. Table XVI shows the conditions and methyl-chloride absorption in three experiments. A horizontal position of the sealed tube was most favorable, permitting best access of CH_3Cl to the solid complex.

TABLE XVI

The $(\text{CH}_3)_3\text{PPCF}_3$ - CH_3Cl Reaction

$(\text{CH}_3)_3\text{PPCF}_3$ (mmoles)	Position of tube	Hours at room temp.	Methyl employed	Chloride (mmoles) absorbed
1.67	vertical	72	8.89	1.23
1.96	horizontal	12	8.14	1.67
3.15	horizontal	72	9.96	3.24

Of the two main volatile products, the more volatile went through a trap at -30°C . under high vacuum, and trapped out at -36°C . Its vapor tensions (e.g. 4.39 mm. at 0°C ., 13.06 mm. at 20°C . and 33.1 mm. at 40°C .) determined the equation $\log_{10}P_{\text{mm}} = 7.635 - 1911/T$; b.p. 129°C .; Trouton constant, 21.7 cal./deg.mole. Samples from two different experiments gave mol. wt. values of 227 and 238, suggesting the biphosphine $(\text{CH}_3\text{PCF}_3)_2$ (calcd. mol. wt. 230). However, this identification must be regarded as uncertain because another sample, made by the action

of a $\text{CH}_3\text{I}-\text{CF}_3\text{PI}_2$ mixture on mercury (as described later) had the right mol. wt. for $(\text{CH}_3\text{PCF}_3)_2$ but was decidedly more volatile. Until the discrepancy is resolved, there can be little confidence in a designation of either product as the true $(\text{CH}_3\text{PCF}_3)_2$.

The less volatile fraction was not difficult to purify, and showed a highly consistent set of vapor tension values, such as 0.80 mm. at 20.0°C . and 10.46 mm. at 53.5°C . However, the sample was destroyed during an attempt to determine the mol. wt. - apparently by the strong catalytic effect of something absorbed in the stop-cock grease. It could have been a triphosphine, but there has been no analysis and in particular the absence of chloride from the formula has not been demonstrated.

In sum, then, the reaction between CH_3Cl and $(\text{CH}_3)_3\text{PPCF}_3$ shows promise of interesting products, but has not been fully studied because of the time needed for other promising work.

The Reaction with Methyl Iodide. An exploratory experiment began with 1.824 mmoles of $(\text{CH}_3)_3\text{PPCF}_3$, which absorbed 1.7 mmoles of CH_3I , rapidly and with noticeable evolution of heat. The resulting white solid began to sublime under high vacuum at 80°C . The reaction was qualitatively different from the methyl chloride addition, as well as much faster; for there was no product which could be distilled at room temperature; the unused methyl iodide was strictly pure. The character of the white solid was tested by treatment with $(\text{CH}_3)_3\text{P}$; had it been a mixture of $(\text{CH}_3)_4\text{PI}$ and CF_3P high-polymers, the latter should have been converted to the equilibrium tetramer-pentamer mixture. Instead, even a six-fold proportion of $(\text{CH}_3)_3\text{P}$ had no effect whatever. An attack by chlorine (2:1 molar ratio, 12 hours at room temperature) formed out of CF_3PCL_2 . Thus it seemed that most of the CF_3P groups were so bound in the solid as to resist the attack by chlorine. An unidentified by-product having mol. wt. 141 might account for some of these CF_3P groups.

The difficulty of bringing the CF_3P groups into reaction led to the hypothesis that the white solid was formed simply by attaching a methyl group to the complex-bonded PCF_3 unit, to make the salt $(\text{CH}_3)_3\text{P}-\text{PCH}_3\text{CF}_3\text{I}^-$. According to this, one might expect that HCl would act to release the CH_3PCF_3 group as the chloride or iodide or both. Accordingly the solid formed by absorption of 3.51 mmoles of CH_3I by 3.53 mmoles of $(\text{CH}_3)_3\text{PPCF}_3$ was treated with 2.30 mmoles of HCl in a sealed tube during 12 hours at room temperature. The HCl was wholly absorbed, forming 0.955 mmole of material having a 0°C . vapor tension of 104 mm. and average molecular weight 148. It was considered that this might be mostly the new compound $\text{CH}_3\text{CF}_3\text{PCL}$ with some CH_3I , so that the best way to isolate the chlorophosphine would be through formation of the corresponding dimethylaminophosphine, $(\text{CH}_3)_2\text{NPCH}_3\text{CF}_3$, from which it could be regained by the action of HCl .

Accordingly, a 0.718 mmole sample of the supposed impure $\text{CH}_3\text{CF}_3\text{PCL}$ was placed with 1.249 mmoles of $(\text{CH}_3)_2\text{NH}$, with reaction on warming to room temperature. A trace of amine was recovered, meaning that the chlorophosphine had not been more than about 85% pure (as already indicated by the low mol. wt.). The resulting aminophosphine was purified by fractional condensation (through a trap at -36°C . and condensing at -45°C .), and amounted to 0.40 mmole. On the basis of these results, the yield of the chlorophosphine might be roughly estimated as about 20%. A considerably better recovery of CH_3PCF_3 was obtained when the method was repeated, as described in the following section.

Chemistry of the CH_3PCF_3 Group

Synthesis of the Aminophosphine. The second experiment on the action of HCl upon the supposed $(\text{CH}_3)_3\text{PPCH}_3\text{CF}_3^+\text{I}^-$ allowed for the possibility that both $\text{CH}_3\text{CF}_3\text{PCl}$ and $\text{CH}_3\text{CF}_3\text{PI}$ would be formed. Hence there was no attempt to isolate either, but the whole volatile product was treated with dimethylamine to make the aminophosphine. This was isolated in pure form and well characterized.

The experiment began with 4.30 mmoles of $(\text{CH}_3)_3\text{PPCF}_3$, which was treated with 26.72 mmoles of CH_3I in a sealed tube. Again the reaction was signalled by a noticeable evolution of heat. After 24 hours, the recovered CH_3I amounted to 21.84 mmoles; used 4.88 mmoles. A trace (about 0.15 mmole) of vapor less volatile than CH_3I also was noticed. The non-volatile solid product, regarded as 4.3 mmoles of $(\text{CH}_3)_3\text{PPCH}_3\text{CF}_3^+\text{I}^-$, was treated with 6.77 mmoles of HCl. The volatile products were removed and the residue treated again with the recovered HCl until no more of this was absorbed; over-all time, 60 hours. The absorption of HCl amounted to 4.16 mmoles, or nearly one HCl per PCF_3 unit originally present.

The volatile products of this HCl reaction included 0.914 mmole of $\text{CH}_3\text{CF}_3\text{PCl}$ and a less volatile fraction which reacted with mercury to form HgI_2 — probably the expected $\text{CH}_3\text{CF}_3\text{PI}$. The two products were treated together with excess $(\text{CH}_3)_2\text{NH}$, yielding 1.97 mmoles of $(\text{CH}_3)_2\text{NPCH}_3\text{CF}_3$, representing 45.8% of the PCF_3 units originally present.

Physical Properties of the Aminophosphine. The new amino compound, presumed to be $(\text{CH}_3)_2\text{NPCH}_3\text{CF}_3$, showed a vapor-phase molecular weight of 160.5 (calcd., 159.1). Further evidence of its identity came from its reaction with HCl, quantitatively forming a compound having the right molecular weight for the chlorophosphine $\text{CH}_3\text{CF}_3\text{PCl}$. The melting point of the aminophosphine could not be observed, because it only formed a glass on cooling to low temperatures. Its vapor tensions (Table XVII) determined the equation $\log_{10} p_{\text{mm}} = 5.9119 - 0.00500T + 1.75 \log_{10} T - 2109/T$ (b.p. 98.9°C .; Trouton constant, 21.0 cal./deg. mole).

TABLE XVII

Vapor Tensions of $(\text{CH}_3)_2\text{NPCH}_3\text{CF}_3$

t ($^\circ\text{C}$.)	0.0	10.5	20.0	24.8	30.0	41.5	64.5
p_{mm} (obsd.)	12.3	22.4	37.1	47.3	61.1	101.8	252.3
p_{mm} (calcd.)	12.3	22.4	37.1	47.2	60.6	101.6	252.4

The infra-red spectrum of $(\text{CH}_3)_2\text{NPCH}_3\text{CF}_3$ showed two very strong peaks at 1177 and 1114 cm^{-1} , just as expected for one CF_3 group on a phosphorus atom. The C-H stretching vibration at 2920 cm^{-1} showed with medium strength, and CH_3 deformations appeared as a medium peak at 1274 and a weak one at 1450 cm^{-1} . A strong band at 978 and two medium ones at 881 and 720 cm^{-1} were not identified.

The Aminophosphine with Diborane. A 0.855 mmole sample of $(\text{CH}_3)_2\text{NPCH}_3\text{CF}_3$ reacted with 0.423 mmole of B_2H_6 to form a slightly volatile liquid having a melting range of -21.6 to 21.3°C . It seemed to be tensiometrically uniform, passing a trap at -10°C . rather slowly, and condensing completely at -25°C . Its vapor tensions in the range 22.5 - 85.3°C . gave a smooth $\log p$ vs. $1/T$ graph which was only roughly described by the equation $\log_{10} p_{\text{mm}} = 8.8363 - 2603.4/T$ (b.p. 164°C .; Trouton constant 26.9 cal./deg.mole), but much better by the Nernst-type equation $\log_{10} p_{\text{mm}} = 9.7396 - 0.009238T + 1.75 \log_{10} T - 3349/T$. However, this would imply a Trouton constant near 17, which is too low to be believable. Hence it is believed that the data were somewhat affected by decomposition. Typical observed pressures were 0.82 mm. at 22.5°C ., 10.52 mm. at 59.9°C ., and 28.43 mm. at 80.0°C .

A 0.160 mmole sample of this adduct, formulated as the BH_3 complex $(\text{CH}_3)_2\text{NPCH}_3\text{CF}_3 \cdot \text{BH}_3$ (without decision as to whether the BH_3 is attached to N or to P), was heated for 12 hours at 160°C . to produce 0.170 mmole of H_2 . This result would correspond to some such reaction as the formation of $\text{CH}_3\text{CF}_3\text{PBH}_2$ polymers and $(\text{CH}_3)_2\text{NH}$, followed by an aminolysis to form an amino-phosphino-borine and hydrogen. Such a reaction would be quite difficult to foresee when $(\text{CH}_3)_2\text{PBH}_2$ polymers are concerned, but might occur far more easily when one of the groups on P is CF_3 . In an attempt to recognize the predicted first stage of the process - the N-P bond splitting to form $(\text{CH}_3)_2\text{NH}$ and polymers of $\text{CH}_3\text{CF}_3\text{PBH}_2$ - a 0.840 mmole sample of the same adduct was heated for 96 hours at 125°C . However, even this relatively mild treatment led to 0.366 mmoles of H_2 . Further studies on this subject are in course.

Conversion to the Chlorophosphine. A 0.258 mmole sample of $(\text{CH}_3)_2\text{NPCH}_3\text{CF}_3$ was exposed at room temperature to 1.40 mmoles of HCl , of which 0.85 mmole was recovered: absorbed, 0.55 mmole (calcd., 0.52). The yield of the supposed $\text{CH}_3\text{CF}_3\text{PCl}$ was 0.250 mmole (calcd., 0.258). These results would accord with the equation



The desired chlorophosphine passed a trap at -78°C . but condensed out completely at -120°C . Its mol. wt. was determined as 151.7 (calcd., 150.5).

Purification and Properties of the Chlorophosphine. For a fuller investigation of the chlorophosphine a larger sample was made by the HCl -conversion from the aminophosphine, but was not easily purified because of the persistence of a trace of HCl , presumably forming an unstable hydrochloride whenever there was an attempt at low-temperature fractionation. Accordingly a small portion of the sample was treated with an even smaller portion of trimethylamine. This produced a non-volatile chloride, which was determined by titration. Thus it was possible to calculate the amount of trimethylamine needed to remove the HCl from the main sample, without introducing an excess of the amine, which would reversibly combine with the chlorophosphine just as HCl does. Now it was possible to get a pure sample of the chlorophosphine by a final fractional condensation. It passed a trap at -70°C . very slowly, and was completely trapped out at -78°C .

The vapor tensions of this sample (Table XVIII) determined the equation $\log_{10} p_{\text{mm}} = 6.04553 - 0.005738T + 1.75 \log_{10} T - 1847.8/T$, which gives the b.p. as 51.1°C . and the Trouton constant as 21.0 cal./deg.mole. The substance has a slight tendency to attack mercury, especially at elevated temperatures. The m.p. of the substance could not be observed.

TABLE XVIII

Vapor Tensions of $\text{CH}_3\text{CF}_3\text{PCl}$

t (°C.)	-45.9	-37.0	-26.0	-7.2	0.00	10.5	21.0
P _{mm} (obsd.)	5.2	10.4	22.0	65.5	94.9	157.3	249.4
P _{mm} (calcd.)	5.4	10.4	21.9	65.5	94.9	157.5	249.2

The infra-red spectrum of $\text{CH}_3\text{CF}_3\text{PCl}$ included a very weak C-H stretching at 2899, weak and medium bands at 1295 and 1417 (attributed to CH_3 -group deformations), and the very strong CF_3 stretchings at 1135 and 1162 cm^{-1} . A medium band at 694, a weak one at 741, and two strong ones at 876 and 903 have not been interpreted.

As a further check on the identity of the chlorophosphine, a 1.432 mmole sample was reconverted by dimethylamine to the aminophosphine $(\text{CH}_3)_2\text{NPCH}_3\text{CF}_3$; yield 1.430 mmoles. In view of the quantitative interconvertibility of these CH_3PCF_3 compounds, and the agreement with the calculated molecular weights, there seems scarcely any doubt that the indicated formulas are correct. However, complete analyses are yet to be done as a final check, and will require the availability of larger supplies of the pertinent materials.

Other Approaches Toward Synthesis. The above method of making CH_3PCF_3 compounds seems fairly devious, so that more direct methods might be preferred. Accordingly we have made a trial of the CF_3PI_2 -Hg reaction in the presence of CH_3I . The experiment employed 5.34 mmoles of CF_3PI_2 with 3.55 mmoles of CH_3I , which were shaken with mercury for three weeks at room temperature. The volatile products were interpreted as

$(\text{CH}_3)_2\text{PCF}_3$ - - - 1.24 mmoles

$(\text{CH}_3\text{PCF}_3)_2$ - - - 0.49 mmole

$(\text{CF}_3\text{P})_{4,5}$ - - - 2.87 mmoles of monomer

According to this, 54% of the CF_3PI_2 went to form CF_3P low polymers, representing no loss because these are easily reconvertible to CF_3PI_2 or used otherwise; and of the remaining 2.47 mmoles of CF_3PI_2 , 40% seemed to represent the desired biphosphine while 50% went to form the relatively useless $(\text{CH}_3)_2\text{PCF}_3$. Experimental conditions more favorable to the supposed biphosphine are yet to be sought.

The $(\text{CH}_3)_2\text{PCF}_3$ was isolated from a trace of CF_3PH_2 through formation of the hydrochloride $(\text{CH}_3)_2\text{PCF}_3 \cdot \text{HCl}$, which proved to be stable only at low temperatures. The HCl was removed from it by triethylamine, and then the $(\text{CH}_3)_2\text{PCF}_3$ could be fully identified by its M.W., vapor tension at 0°C., and infra-red spectrum.

The hypothetical biphosphine $(\text{CH}_3\text{PCF}_3)_2$ was purified by fractional condensation, passing a trap at -40°C. and condensing at -45°C. Its vapor-phase molecular weight was determined as 232 (calcd., 230) and a preliminary set of vapor tensions

in the range 0°C. (7.35 mm.) to 75.2°C. (170.9 mm.) showed a good correlation with the equation $\log_{10}P_{\text{mm}} = 7.1173 - 1699/T$. This would give the b.p. as 128°C.; however, the low value of the Trouton constant (19.9 cal./deg.mole) suggests some uncertainty in regard to impurities. Also, the volatility throughout the measured range is well above that of the supposed $(\text{CH}_3\text{PCF}_3)_2$ obtained from the $\text{CH}_3\text{Cl}-(\text{CH}_3)_3\text{PPCF}_3$ reaction. Reconciliation of the two approaches will require more work.

In yet another new approach, it was considered possible that a compound of the type $(\text{CH}_3)_2\text{NPCF}_3\text{X}$ might be methylated by a suitable reagent, just as $(\text{CH}_3)_2\text{NPCI}_2$ was methylated by the Grignard CH_3MgBr to make $(\text{CH}_3)_2\text{NP}(\text{CH}_3)_2$. In the first trial of this idea, CF_3PI_2 was brought to reaction with $2(\text{CH}_3)_2\text{NH}$, but it was not feasible to isolate the expected $(\text{CH}_3)_2\text{NPCF}_3\text{I}$. Hence the volatile components were treated with $2\text{Zn}(\text{CH}_3)_2$, of which 73% could be recovered after the reaction. The yield of the tertiary phosphine $(\text{CH}_3)_2\text{PCF}_3$ was 6% (based on CF_3 groups), and there was even less of a fraction having M.W. 190 (v.t. 2.5 mm. at 0°C.).

For a more controlled experiment, it was considered well to employ the dichloride CF_3PCL_2 instead of the diiodide, so that the intermediate amino-chloro-phosphine could be isolated. Accordingly a sample of CF_3PI_2 was converted to CF_3PCL_2 by the action of AgCl (75% yield). Then 1.92 mmoles of CF_3PCL_2 and 2.67 mmoles of $(\text{CH}_3)_2\text{NH}$ (an intentional deficiency) were mixed to produce 0.92 mmole of $(\text{CH}_3)_2\text{NPCF}_3\text{Cl}$, with recovery of 0.473 mmole of CF_3PCL_2 and no amine. Thus the yield of the desired amino-chloro-phosphine was 63% of the dichloride, the loss being attributable to some formation of a bis-amino-phosphine.

The reaction of $(\text{CH}_3)_2\text{NPCF}_3\text{Cl}$ with $\text{Zn}(\text{CH}_3)_2$ gave none of the desired methyl compound, probably because of complex-formation between the $(\text{CH}_3)_2\text{N}$ unit and the zinc ion. However, before the experiment was tried, it was possible to prove the formula of the new amino-chloro-phosphine and to demonstrate its purity by a consistent set of vapor tensions.

The Compound $(\text{CH}_3)_2\text{NPCF}_3\text{Cl}$. The volatile amine- CF_3PCL_2 reaction-product was purified by fractional condensation, passing a trap at -36°C. and condensing at -45°C. Its M.W. in the vapor phase at 69.4°C. was 180.7; calcd., 179.5. The formula was further confirmed by the reaction of 0.494 mmole of the substance with HCl in excess (1.043 mmole), giving 0.484 mmole of CF_3PCL_2 and 0.504 mmole of $(\text{CH}_3)_2\text{NH}_2\text{Cl}$.

The vapor tensions (Table XIX) were correlated by the equation $\log_{10}P_{\text{mm}} = 5.32310 - 0.0038T + 1.75 \log_{10}T - 2134/T$; b.p. 115.0°C. and Trouton constant 22.0 cal./deg.mole.

TABLE XIX

Vapor Tensions of $(\text{CH}_3)_2\text{NPCF}_3\text{Cl}$

t (°C.)	0.00	5.4	29.4	40.0	50.2	59.7	69.7	74.9
P_{mm} (obsd.)	5.47	7.61	29.03	48.48	77.06	115.67	170.75	207.70
P_{mm} (calcd.)	5.45	7.63	28.94	48.56	77.06	115.57	170.84	207.60

CHAPTER VI

CHEMISTRY OF FLUOROCARBON POLYPHOSPHINES

Diphosphines of the type $R_2P-C_n-PR_2$, where carbon holds either hydrogen or fluorine, are of interest both practically and theoretically. The hydrocarbon types are very strong bases which can be used for making phosphorus-boron resins with a possibility of internal cross-linking. The fluorocarbon types can be extended to make $(-P-C_n-)_x$ polymers when enough is known of this kind of chemistry so that syntheses and structural interpretations become possible. Also, when such polymers can be made with good knowledge of their character, the way will be open for extension to the more stable oxidized and nitridized forms. A similar extension of the hydrocarbon polyphosphine chemistry may be farther away, but should not be left out of consideration.

Until recently there has been little published work on such carbon-connected diphosphines. Aside from the considerable use of the Wagner and Burg procedure for alkylation of phosphinides¹⁹ in the laboratories of the Prime Contractor, the same method has been used recently by Wymore to make $(C_2H_5)_2PC_2H_4P(C_2H_5)_2$ ²⁰ and by Leffler and Teach to make $H_2PC_3H_6PH_2$.²¹ Also Hitchcock and Mann have had occasion to make $C_2H_5C_6H_5PC_2H_4PC_2H_5C_6H_5$ as an incident in their pursuit of heterocyclic phosphine chemistry;²² and Parshall, England, and Lindsay recently reported the addition of phosphine to C_2F_4 to make $H_2PC_2F_4PH_2$.²³

During the past year our knowledge of this class of polyphosphines has advanced through further studies of the reactions of the biphosphine $P_2(CF_3)_4$ with C_2H_4 , C_2F_4 , and C_2H_2 . All of these reactions proved to be more complex than a simple addition to pi bonds; and their various products offer numerous opportunities of rich new developments in phosphine chemistry. For such studies the biphosphine $P_2(CF_3)_4$ seems to be especially advantageous because it reacts either spontaneously, as with ethylene, or with the aid of a catalytic trace of iodine, as with C_2F_4 or with C_2H_2 . Most of the products are volatile enough for easy manipulation by quantitative high-vacuum methods, and their properties furnish the basis for useful speculations concerning other polyphosphines which might be desirable.

The Biphosphine-Ethylene Reaction

The previously-reported room-temperature reaction between $P_2(CF_3)_4$ and C_2H_4 seemed fairly simple because the yield of the diphosphine $(CF_3)_2PC_2H_4P(CF_3)_2$ was nearly 95% (Ref. 4, p. 91). More recently, however, we have performed the reaction during 65 hours at 65°C. (with 1.913 mmoles of the biphosphine and 2.968 mmoles of C_2H_4), obtaining only an 88% yield of the biphosphine. The improved yield of the by-products made it feasible to isolate them and to recognize the character of the side-reactions. The results are summarized in Table XX. Yet another reaction product was a trace of a colorless non-volatile oil, the empirical formula of which was indicated by the stoichiometry as $(CF_3)_9P_6(C_2H_4)_5$. This might be a mixture of $(CF_3)_2P(-PC_2H_4-)_nP(CF_3)_2$ chains in which n averages five.

CF_3

The acetylene reaction (see below) seems to form an analogous chain.

TABLE XX

The $P_2(CF_3)_4-C_2H_4$ Reaction at 65°C.

Substance	Amount (mmoles)	Volatility (mm./t°C.)	Mol. Wt.		Remarks
			found	calcd.	
C_2H_4 recovered used up	1.405 1.563	-	28.1	28.05	-
$P_2(CF_3)_4$ recovered used up	0.354 1.559	22 mm./0°	335.3	338.0	-
$(CF_3)_3P$	0.107	3 mm./-78°	239.2	238.0	Checked by infra-red
$(CF_3)_2PC_2H_4P(CF_3)_2$	1.372	1.30 mm./0°	366.4 365.6	366.0 ₅	88.0% yield
$[(CF_3)_2PC_2H_4]_2PCF_3$	0.060	0.20 mm./24°	479	494	-

The formation of $=PCF_3$ compounds and $(CF_3)_3P$ surely cannot be ascribed to a decomposition of $(CF_3)_2PC_2H_4P(CF_3)_2$ (at 65°C.) for this diphosphine proved to be reasonably stable at 240°C., giving only a 2% yield of more volatile products after 69 hours at that temperature. However, an 8-day heating at 285°C. caused a 27% decomposition, with 7.8% of the P going to $(CF_3)_3P$ and 4.5% of the CF_3 groups appearing as HCF_3 . The only other product was a brown deposit on the walls of the containing tube. Since it is so difficult to move CF_3 groups from one phosphorus atom to another in this diphosphine, and even more difficult to do so in $P_2(CF_3)_4$ (300°C. or higher), it seems that ethylene has a special effectiveness in causing such a CF_3 -group transfer. This effect seems to be general for nucleophilic agents such as ethylene or iodine, which seemed to cause CF_3 -group migration also in other reactions yet to be described.

The Biphosphine-Ethylene Reaction in the Dark. In view of the analogy of the $P_2(CF_3)_4-C_2H_4$ reaction to the addition of chlorine to ethylene, it seemed possible that light might affect its rate. In order to test this idea, a mixture of 2.338 mmoles of $P_2(CF_3)_4$ and 2.041 mmoles of C_2H_4 was stored for 13 days in a black-painted sealed tube at room temperature. The results (Table XXI) show that light has some effect, for a parallel experiment, going for 11 days in ordinary daylight, showed a 97% conversion in contrast to a 48% conversion of the $P_2(CF_3)_4$ here observed. It is also interesting that the yield of $(CF_3)_3P$ per mole of used-up $P_2(CF_3)_4$ was only four-tenths as great in the dark reaction as in the light; however, we do not yet know whether this interesting side reaction is especially promoted by light, or is more characteristic of the terminal stages of the over-all reaction.

TABLE XXI

Dark $P_2(CF_3)_4-C_2H_4$ Reaction at Room Temperature

Substance	Amount (mmoles)	Volatility (mm./t°C.)	Mol. Wt.		Remarks
			found	calcd.	
C_2H_4 { recovered used up	0.905 1.136	-	28.9	28.1	-
$P_2(CF_3)_4$ { recovered used up	1.207 1.131	22 mm./0°	338.5	338.0	-
$(CF_3)_3P$	0.032	-	-	-	{ Checked by infra-red
$(CF_3)_2PC_2H_4P(CF_3)_2$	1.088	1.28 mm./0°	366.4	366.05	{ 96% yield from 48% conversion
(Less volatile)	(5.5 mg.)	-	-	-	-

Physical Properties of the Diphosphine. A highly purified sample of $(CF_3)_2PC_2H_4P(CF_3)_2$ melted in the very narrow range -51.4 to $-51.3^\circ C$. The representative vapor tensions shown in Table XXII determined the equation $\log_{10} p_{mm} = 8.0982 - 0.00700T + 1.75 \log_{10} T - 2827/T$, from which the b.p. is calculated as $134.7^\circ C$. and the Trouton constant 22.3 cal./deg.mole. This conformity to a reasonable equation, taken with the very sharp melting range, would indicate a fairly high purity. The nearly quantitative synthesis and the agreement of the molecular-weight results with the calculated values are enough to confirm the formula $(CF_3)_2PC_2H_4P(CF_3)_2$.

TABLE XXII

Vapor Tensions of $(CF_3)_2PC_2H_4P(CF_3)_2$

t (°C.)	0.00	20.2	30.2	40.4	49.7	60.3	68.8	80.2
p_{mm} (obsd.)	1.30	5.36	9.94	18.12	29.69	50.24	74.4	121.5
p_{mm} (calcd.)	1.26	5.32	9.98	18.03	29.70	50.29	74.5	121.3

The Diphosphine with Diborane. The attachment of a hydrocarbon group to the $(CF_3)_2P$ group should give phosphorus a tendency toward base action somewhat stronger than that found for $(CF_3)_2PH$.²⁴ However, when this effect was tested by means of diborane, there was no rapid adduct-formation, but only a slow reaction at room temperature. In an attempt to push the reaction forward, the mixture was heated for 9 days in a sealed tube at $63^\circ C$., with the results shown in Table XXIII.

TABLE XXIII

The $(\text{CF}_3)_2\text{PC}_2\text{H}_4\text{P}(\text{CF}_3)_2$ - B_2H_6 Reaction at 63°C .

Substance	Amount (mmoles)	Volatility (mm./t°C.)	Mol. Wt.		Infra-Red
			found	calcd.	
$(\text{CF}_3)_2\text{PC}_2\text{H}_4\text{P}(\text{CF}_3)_2$ employed:	0.537	-	-	-	-
recovered:	0.407	1.30 mm./t°C.	365.3	366.05	-
used up (24%):	0.130				
B_2H_6 employed:	0.688	-	-	-	-
recovered:	0.150	-	27.3	27.7	Checked
used up:	0.538	-	-	-	-
B_5H_9 found	0.048	-	62.4	63.2	Checked

The non-volatile product was a nearly colorless oil. The material balance gives for it the average empirical formula $\text{B}_{8.5}\text{H}_{8.9}(\text{CF}_3)_2\text{PC}_2\text{H}_4\text{P}(\text{CF}_3)_2$. This seems to be closely related to the resins formed from other tertiary phosphines with B_5H_9 (Cf. Chapter I and Ref. 3, p. 12). By comparison with the $(\text{CH}_3)_3\text{P}$ case, the ratio of boron and B-H hydrogen to phosphorus here would suggest that about 30% of the diphosphine molecules are using both phosphorus atoms for electron-donor bonding to boron. However, there is another way to explain the high ratio of BH to diphosphine molecules: if the donor-bonding of P to B is as weak as might be expected, it may be that the boron-hydride polymer network simply makes fewer bonds to the diphosphine (employed unfunctionally) than in the case of $(\text{CH}_3)_3\text{P}$.

In another test of the donor-bonding power of phosphorus in this situation, the diphosphine proved to be inert toward methyl iodide, forming no adduct even during four days at 105°C .

The Biphosphine-Tetrafluoroethylene Reaction

The easy and nearly quantitative addition of $\text{P}_2(\text{CF}_3)_4$ into the double bond of ethylene raised the question of how generally applicable this type of reaction might be. As an extreme test of this question, the reaction of $\text{P}_2(\text{CF}_3)_4$ with C_2F_4 was tried. In this case it was far more difficult to cause the reaction. The mixture was changed by heating for 150 hours at 205°C ., but the products were very difficult to resolve. Both $(\text{CH}_3)_3\text{P}$ and BF_3 proved to be ineffective as catalysts at temperatures up to 75°C . It may be reasonable to infer that the addition of $\text{P}_2(\text{CF}_3)_4$ to C_2H_4 depends upon an initial electron-donor action by the ethylene. Such action by C_2F_4 would be far weaker and surely not improved by BF_3 , nor sufficiently by the basic effect of $(\text{CH}_3)_3\text{P}$. However, a small crystal of iodine was used quite successfully as a catalyst. This catalyst probably works in two distinct ways: to break the biphosphine down into $(\text{CF}_3)_2\text{PI}$ for addition to the double bond of C_2F_4 , or to add itself directly to the C_2F_4 to make $\text{C}_2\text{F}_4\text{I}_2$. In the former case, one would get $(\text{CF}_3)_2\text{PC}_2\text{F}_4\text{I}$, which might well be expected to react with more $\text{P}_2(\text{CF}_3)_4$ to give the desired $(\text{CF}_3)_2\text{C}_2\text{F}_4\text{P}(\text{CF}_3)_2$ and more $(\text{CF}_3)_2\text{PI}$ to repeat the

process. Or, at a high enough temperature, either $C_2F_4I_2$ could add its C-I bond into the C_2F_4 double bond to start a polymer chain, or $(CF_3)_2PC_2F_4I$ could do the same. In order to minimize the side effects, the temperature was limited to $165^\circ C$.

During 34 hours at that temperature, 2.646 mmoles of the biphosphine $P_2(CF_3)_4$ and 3.334 mmoles of C_2F_4 (with a tiny crystal of iodine) produced a mixture which was freed of any reactive iodides by the action of mercury. Then the volatile components were separated into the fractions shown in Table XXIV.

TABLE XXIV

Components from the Reaction of $P_2(CF_3)_4$ with C_2F_4

Substance	Yield (mmoles)	Volatility	Mol. wt.		Further evidence of identity
			found	calcd.	
C_2F_4 recovered used up	0.608 2.726	62 mm. at $-111.9^\circ C$.	100.0	100.0 ₂	-
$P_2(CF_3)_4$ recovered used up	0.782 1.864	22 mm./ 0°	337.3	338.0	-
cyclo- C_4F_8	0.019	Passed $-110^\circ C$.	196	200	I.R. spectrum
$(CF_3)_3P + C_4F_8$	0.421	3 mm./ -78°	223	-	I.R. spectrum showed both
cyclo- $C_4F_8PCF_3$ and $(CF_3)_3P$	0.504	nil/ -90°	300	-	Many; see text
Unidentified	0.083	8 mm./ 0°	415	-	-
$(CF_3)_2PC_2F_4P(CF_3)_2$ (m.p. $-49.6^\circ C$.)	1.092 (59%)	2.13 mm. at $0^\circ C$.	438.1 440.8	438	Many; see text
Unidentified	-	non-vol.	-	-	-

Thus the reaction used up 1.46 C_2F_4 per $P_2(CF_3)_4$, as might be expected if there were some lengthening of the fluorocarbon chain. Apparently there was little lengthening beyond two C_2F_4 units, for the volatile compounds containing C_2F_4 and C_4F_8 units accounted for virtually all of the used-up C_2F_4 . The individual new compounds here produced are discussed in more detail in the following sections.

The Perfluoro-Diphosphine. The new compound $(CF_3)_2PC_2F_4P(CF_3)_2$ melted sharply: -49.7 to $-49.6^\circ C$. Its vapor tensions, shown in Table XXV, determined the equation $\log_{10}P_{\text{mm}} = 7.2311 + 1.75 \log_{10}T - 0.005996T - 2603/T$ (b.p. $127.0^\circ C$; Trouton constant 22.1 cal./deg.mole).

TABLE XXV

Vapor Tensions of $(\text{CF}_3)_2\text{PC}_2\text{F}_4\text{P}(\text{CF}_3)_2$

t (°C.)	p_{mm} (obsd.)	p_{mm} (calcd.)		t	p (obsd.)	p (calcd.)
0.00	2.13	2.13		47.5	37.79	37.78
12.8	5.13	5.17		52.4	48.19	48.03
21.5	9.00	8.97		61.3	72.6	72.6
31.2	15.97	15.87		66.0	89.5	89.5
36.4	21.21	21.18		70.7	109.3	109.3

The basic hydrolysis of a 0.416 mmole sample (10% NaOH, 16 hours at room temperature) gave 3.88 HCF_3 and 0.97 $\text{H}_2\text{C}_2\text{F}_4$ per molecule - perhaps a slightly incomplete reaction, but giving a perfect 4:1 ratio of the two hydro-fluorocarbons. Both were identified beyond doubt by their infra-red spectra, the one for 1,1,2,2-tetrafluoroethane having been obtained from the record submitted by Hazeldine and Marklow to the Chemical Society. Its b.p. also was checked: found, 19.5°C. vs. 20°C. reported by Hazeldine and Marklow.²⁵ The mol. wt. of this compound was determined as 102.0; calcd., 102.04. Thus the basic hydrolysis of the diphosphine gave the right fluorinated hydrocarbons in nearly the amounts required by the formula $(\text{CF}_3)_2\text{PC}_2\text{F}_4\text{P}(\text{CF}_3)_2$, which now may be taken as certain.

The Perfluoro-Cyclo-Butane. The material designated as cyclo- C_4F_8 in Table XXIV - a 0.019 mmole fraction passing a trap at -110°C. but condensed out at -140°C. - had an infra-red spectrum accurately fitting the known picture.²⁶ This fact, taken with an approximately correct molecular weight result, leaves no doubt that the material is the C_4F_8 ring compound. Its formation is an example of the effect of iodine toward the polymerization of C_2F_4 .

A slightly less volatile fraction (0.421 mmole) showed infra-red absorption peaks characteristic of both $(\text{CF}_3)_3\text{P}$ and C_4F_8 . The average molecular weight value, 223, would suggest a 60:40 mixture of these components. Thus the total yield of the C_4F_8 is estimated as 0.19 mmole, representing nearly 7% of the consumed C_2F_4 .

The presence of $(\text{CF}_3)_3\text{P}$ here and in the following fraction is evidence of migration of CF_3 groups from one phosphorus atom to another. This is not unexpected, for iodine is known to convert $\text{P}_2(\text{CF}_3)_4$ to $(\text{CF}_3)_2\text{PI}$, and the inter-conversion of the $\text{CF}_3\text{-P-I}$ compounds is known.

The Cyclophosphine Fraction. The following fraction was roughly isolated by means of a micro-fractionating-column operating under high vacuum with a reflux temperature of -78°C., and then further purified by fractional condensation. Then the molecular weight determinations gave 300.5 and 300.2. This fraction could not be $(\text{CF}_3)_2\text{PI}$ (M.W. 296), for it would not react with mercury. The ring C_6F_{12} (M.W. 300) seemed to be ruled out by the infra-red spectrum, which was much like that of

cyclo-C₄F₈ except for an extra band at 1000 cm.⁻¹. Hence the best way to understand a molecular weight near 300 seemed to be the cyclic phosphine CF₃PC₄F₈, the presence of which would be reasonable in view of the demonstration that CF₃ groups are mobile from and to (CF₃)₂P groups in the main reaction, and the expectation of C₄F₈I₂ as a reaction intermediate.

In spite of the close agreement of the molecular weight, this fraction was assumed to have some (CF₃)₃P as an impurity, for the infra-red spectrum included lines characteristic of this and the basic hydrolysis later seemed to confirm its presence. However, no amount of fractionation seemed to improve the purity. An attempt to make a separation by forming a BH₃ complex also failed, because no complex could be formed. The fact that no further purification could be achieved by more distillation is indicated by the agreement of a set of vapor tensions with the equation $\log_{10} p_{\text{mm}} = 7.8628 - 1692/T$ (b.p. 67°C.; Trouton constant 22.8 cal./deg.mole), as shown in Table XXVI.

TABLE XXVI

Vapor Tensions of the Supposed CF₃PC₄F₈ Fraction

t (°C.)	-21.7	-14.3	0.00	5.3	11.1	19.7
p _{mm} (obsd.)	13.6	21.0	47.3	62.2	81.8	121.1
p _{mm} (calcd.)	13.6	21.2	46.7	61.2	81.4	121.7

The ultra-violet spectrum of this fraction showed no structure; only a steadily increasing absorption from 2300 to 1900 Å., with at most a slight shoulder near 2000 Å. Hence there could be no P-P nor vinyl-P bonding in the sample.

The basic hydrolysis of a 0.287 mmole portion of this material (10% NaOH, 19 hours at room temperature) yielded 0.400 mmole of HCF₃ but only 0.210 mmole of H₂C₄F₈, respectively 140% and 73% of the amounts expected for complete hydrolysis of pure CF₃PC₄F₈. The detachment of P-C bonds thus amounted to 0.820 mmoles, or better than 95% of the expected 0.861. Assuming that the minor incompleteness of the reaction affected the yields of HCF₃ and H₂C₄F₈ equally, these results would imply a mixture of 76 mole percent CF₃PC₄F₈ and 24 mole percent (CF₃)₃P. The difficulty is that so much (CF₃)₃P would require a molecular weight around 285 instead of the observed 300. The discrepancy is yet to be resolved; but the formation of H₂C₄F₈ (the infra-red spectrum of which agreed with the literature)²⁷ does make a strong argument for the presence of CF₃PC₄F₈ as a major part of the sample.

Discussion. It is apparent that the main reaction here was the addition of P₂(CF₃)₄ to the double bond of C₂F₄, to produce a diphosphine analogous to that obtained when ethylene was used. The success of this catalyzed reaction, even with such an extreme of electronegativity as that represented by C₂F₄, means that it should be possible to accomplish similar results with a wide range of olefines, using appropriate catalysts.

The connection of two phosphorus atoms by the C_2F_4 unit represents a definite step toward high polymers based upon a $(=PC_2F_4-)_n$ skeleton. For example, one way to utilize the new diphosphine $(CF_3)_2PC_2F_4P(CF_3)_2$ would be to heat it with a catalytic portion of iodine, in order to exchange P-C bonds. Some occurrence of this process may well account for much of the non-volatile product of the present experiment; to this product, the rough reaction balance would assign about 0.7 mmole of $(CF_3)_2P$ groups and 0.5 mmole of C_2F_4 . Another approach to polymers would be to heat the diphosphine with phosphorus, for results which are implied by the experiment described in the following paragraph. Both methods could be employed also for converting $CF_3PC_4F_8$ to polymeric forms. To a large extent it would be possible to avoid cross-linking in the resulting polymers, so that they could be dissolved for conversion to pentavalent phosphorus polymers having high oxidative stability. However, there is much chemistry yet to be learned in order to plan the formation of such polymers, especially with control of cross-linking.

Tris(trifluoromethyl)phosphine with Phosphorus. The first reason for trying the reaction of $(CF_3)_3P$ with P_4 was a hope of direct formation of $P_2(CF_3)_4$ and CF_3P polymers, thus deriving an advantage from the otherwise useless by-product $(CF_3)_3P$. However, the same experiment, which did produce some $P_2(CF_3)_4$, serves also as an example of a method whereby more complicated tertiary fluoro-carbon-phosphines might be converted to polymers. It was known that $(CF_3)_3P$ reacts with iodine to make $(CF_3)_2PI$ and CF_3PI_2 ; and it seemed possible that these would react with phosphorus to make $P_2(CF_3)_4$ and $(CF_3P)_n$, leaving P-I compounds to react with more $(CF_3)_3P$. Thus a trace of iodine would be a catalyst for the desired $P_4-(CF_3)_3P$ reaction.

Accordingly 2.00 mmoles of $(CF_3)_3P$ and 4.93 mmoles of thoroughly dried red phosphorus, with a trace of sublimed-in iodine, were heated in a sealed Pyrex tube. There seemed to be no reaction during 24 hours at $150^\circ C.$, but extensive progress occurred during 75 hours at $200^\circ C.$ The mixture was fractionated to yield the following substances:

$(CF_3)_3P$ - - - 1.63 mmoles (used, 0.37 mmole)

$P_2(CF_3)_4$ - - - 0.186 mmole (M.W. 332; 23 mm./ $0^\circ C.$)

HCF_3 - - - - - 0.109 mmole (H from stop-cock grease)

Thus the yield of $P_2(CF_3)_4$ was quite gratifying in relation to the amount of $(CF_3)_3P$ consumed. For practical purposes, however, it would be desirable to increase the speed of the process. It is not yet known whether some $(CF_3P)_n$ might be obtained by pushing the reaction farther.

The Biphosphine-Acetylene Reaction

Like tetrafluoroethylene, acetylene requires a catalyst for reaction with $P_2(CF_3)_4$. Again $(CH_3)_3P$ and BF_3 had no effect, but a trace of iodine promoted a complex reaction well enough, leading to a 58% yield of the interesting new 1,2-diphosphinoethylene $(CF_3)_2PC_2H_2P(CF_3)_2$ and lesser yields of by-products implying migration of CF_3 groups. The initial experiment, using 2.386 mmoles of $P_2(CF_3)_4$ with 2.595 mmoles of C_2H_2 (93 hours at $93^\circ C.$, with a tiny crystal of iodine) consumed 1.525 mmoles of $P_2(CF_3)_4$ and 1.668 mmoles of C_2H_2 , producing 0.966 mmole of $(CF_3)_2PC_2H_2P(CF_3)_2$. This represents 58% of the consumed C_2H_2 of 63% of the consumed $P_2(CF_3)_4$.

The by-products were more fully explored in a larger experiment, the details of which are summarized in Table XXVII. Here, as in the initial experiment, any active iodides were removed by shaking with mercury before the volatiles were separated by distillation methods in the high-vacuum apparatus. The sealed-tube heating went for 67 hours at 100°C.

TABLE XXVII

Components from the Reaction of $P_2(CF_3)_4$ with C_2H_2

Substance	Yield (mmoles)	Volatility (mm. at t°C.)	Mol. wt.		Further Evidence of Identity
			found	calcd.	
C_2H_2 recovered used up	0.369 5.162	-	27.7	26.0	I.R. Spectrum
$P_2(CF_3)_4$ recovered used up	0.216 4.753	22 mm./0°	337.8	338.0	-
$(CF_3)_3P$	0.635	3 mm./-78°	238	238	I.R. Spectrum
$(CF_3)_2PC_2H_2CF_3$	0.310	43 mm./0°	263	264	I.R.; see text
$(CF_3)_2PC_2H_2P(CF_3)_2$ (m.p. -54°C.)	2.937 (57%)	2.3 mm./0°	364.5 364.1	364.0	I.R.; see text
Unidentified	0.096	2.3 mm./27°	408	-	-
Unidentified	0.057	1.1 mm./35°	454	-	-
$CF_3P[C_2H_2P(CF_3)_2]_2$ (liquid)	0.193	0.22 mm./24°	481	490	I.R.; see text
Unidentified	-	non-vol. oil	-	-	-

The more detailed study of these products and their consequences will appear in the following sections.

The Diphosphinoethylene. As in the C_2F_4 addition, the major product here was the expected product of adding the biphosphine into the pi bond, namely the interesting and very probably useful diphosphine $(CF_3)_2PC_2H_2P(CF_3)_2$. The yield of this represented 57% of the consumed acetylene or 62% of the consumed $P_2(CF_3)_4$. The molecular formula, already indicated by the molecular-weight determinations (Table XXVII), was virtually confirmed by the basic hydrolysis (0.262 mmole, 13 hrs. at room temperature; 24 hrs. at 100°C.), giving 3.54 HCF_3 per molecule. The deviation from the ideal 4.00 HCF_3 per molecule is usual for CF_3 -phosphines with at least one hydrocarbon group on phosphorus. A somewhat better CF_3 -group analysis was obtained by the reaction of a sample with iodine; Cf. the iodine method of analysis, below.

The vapor tensions of the diphosphinoethylene, shown in Table XXVIII, determine the equation $\log_{10}P_{\text{mm}} = 7.3690 + 1.75 \log T - 0.006009T - 2631/T$ (b.p. 122.0°C.; Trouton constant, 23.0 cal./deg.mole.) As indicated in Table XXVII, its m.p. was observed as -54°C.

TABLE XXVIII

Vapor Tensions of $(\text{CF}_3)_2\text{PC}_2\text{H}_2\text{P}(\text{CF}_3)_2$

t (°C.)	0.00	4.5	19.6	25.8	31.6	36.4	51.8	61.0
P_{mm} (obsd.)	2.29	3.20	8.60	12.81	17.89	23.42	52.12	80.4
P_{mm} (calcd.)	2.30	3.18	8.65	12.75	17.88	23.41	52.07	80.4

The ultra-violet spectrum of the diphosphino-ethylene has a peak at 2295 Å. (ext. coeff. $\epsilon = 3560$) and minimum at 2115 Å. ($\epsilon = 2600$). The ethylene pi cloud would be expected to extend into the phosphorus atoms, bringing the peak conveniently into the quartz region.

Infra-Red Spectrum of the Diphosphino-ethylene. The infra-red spectrum of $(\text{CF}_3)_2\text{PC}_2\text{H}_2\text{P}(\text{CF}_3)_2$ showed the expected pattern of C-F vibrations, but was of more interest in relation to the question of cis-trans isomerism. A one-meter cell was used, (with the Infracord instrument), for sufficient intensity on a vapor which could not be brought to high pressure. Even so, it was not possible to detect any band in the 6 micron region, such as would correspond to the C=C stretching vibration. This would mean a virtual absence of polarity effects due to the C=C stretching, and this requires the center of symmetry shown by the trans- isomer. Also favoring the trans- isomer is the appearance of a band corresponding to a C-H out-of-plane vibration, which is commonly used to distinguish between cis- and trans- isomers of olefine hydrocarbons. In fluorinated olefines and their derivatives, this band (near 10.36 microns) is more variable as to position, but still can be used diagnostically, according to Haszeldine.²⁸

The assignable peaks of the spectrum are shown by Table XXIX.

The absence of a C-H stretching band need not be taken amiss, for such bands have been found to be very weak in many $\text{RC}_2\text{H}_2\text{R}$ compounds.

TABLE XXIX

Infra-Red Spectrum of $(\text{CF}_3)_2\text{PC}_2\text{H}_2\text{P}(\text{CF}_3)_2$

Frequency (cm^{-1})	Intensity	Assignment	Literature Range (Bellamy)
987	medium	C-H out-of-plane deformation	970-960 cm^{-1} for trans-olefines
1133 1147 1179 1193	all very strong	C-F stretching	(similar to these)
1287	medium	C-H in-plane deformation; less probably C-F stretching	1310-1295 cm^{-1} for trans-olefines

The Diborane-Diphosphinoethylene Reaction Product. The olefinic double bond at the center of the molecule $(\text{CF}_3)_2\text{PC}_2\text{H}_2\text{P}(\text{CF}_3)_2$ was indicated by its absorption of one BH_3 group from a slightly excessive sample of diborane. The 0.371 mmole sample of the ethylenic diphosphine added 0.195 mmole of B_2H_6 , corresponding to 0.53 BH_3 per $(\text{CF}_3)_2\text{PC}_2\text{H}_2\text{P}(\text{CF}_3)_2$, during 17 hours in a sealed tube at room temperature. Evidently the BH_3 group went into the double bond in the normal manner - BH_2 attached to one C and H to the other - for the non-volatile product, reacting with methanol and HCl during 19 hours at 100°C ., gave 0.769 mmole of H_2 , representing 1.97 active H per B or 2.07 active H per diphosphine molecule. Thus the formula of the substance should be written empirically as an RBH_2 type rather than as a phosphine- BH_3 complex.

Further evidence that the material is not a phosphine- BH_3 complex was found in its failure to lose a BH_3 group on contact with trimethylamine. A sample of the adduct, made from 0.608 mmole of $(\text{CF}_3)_2\text{PC}_2\text{H}_2\text{P}(\text{CF}_3)_2$ and 0.302 mmole of B_2H_6 , was exposed 1.306 mmole of $(\text{CH}_3)_3\text{N}$ (681 mm. at 0°C .) in a sealed Pyrex tube. The mixture appeared as a slightly cloudy solution at room temperature. A week later, the tube was opened and 0.693 mmole of $(\text{CH}_3)_3\text{N}$ was recovered. Thus 0.613 mmole of the amine remained with 0.608 mmole of the RBH_2 material, and there was no trace of the volatile $(\text{CH}_3)_3\text{NBH}_3$. Evidently a complex of the type $\text{RBH}_2 \cdot (\text{CH}_3)_3\text{N}$ had formed, and was not appreciably volatile.

The structural formulation of this boron-hydride derivative is a matter of several alternatives. As an RBH_2 type it might be expected to form a $\begin{array}{c} \text{H} \cdot \\ \cdot \text{B} \cdot \text{B} \cdot \\ \cdot \text{H} \end{array}$ bridged dimer - a 1,2- substituted diborane. However, on inspection of the monomer formula $(\text{CF}_3)_2\text{P}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{P}(\text{CF}_3)_2$ it is apparent that a donor-acceptor bond between

boron and the far P atom would give a four-atom ring to stabilize the monomer. Or, P-B dative bonding between molecules could form a dimer having a $(PCB)_2$ hexatomic ring, a $(PCCB)_2$ eight-atom ring, or even a $(PCCBPCB)$ seven-atom ring. The same principle, of course, could lead to higher polymers, such as one might suspect to be present in a substance which we found to be nearly insoluble in a number of common organic solvents. It proved to be soluble in diethyl ether to the extent of a half mole percent, with indications of the monomer form which ether-complexing would support.

The first positive evidence concerning the constitution of $(CF_3)_2PCH_2CHBH_2P(CF_3)_2$ was obtained from its infra-red spectrum, which suggests a monomer-dimer equilibrium of the type $2RBH_2 \rightleftharpoons (RBH_2)_2$. The air-reactive sample was enclosed within a KBr pellet and the spectrum was recorded by the Infracord instrument. Table XXX shows the recorded frequencies beyond those already found (Table XXIX) for the parent compound, $(CF_3)_2PC_2H_2P(CF_3)_2$.

TABLE XXX

Infra-Red Spectrum of $(CF_3)_2PCH_2CHBH_2P(CF_3)_2$

(Frequencies additional to Table XXIX)

Frequency (cm. ⁻¹)	Intensity	Assignment	Reference
2900	Weak	C-H stretch	Bellamy
2438	Strong	B-H _t stretch	Shapiro ²⁹
2381	Strong	B-H _t stretch	Shapiro ²⁹
1626	Medium	B-H _b stretch	Shapiro ²⁹
1383	Very str.	B-O stretch	Lehmann ³⁰
1040	Very str.	Uncertain	-
1013	Strong	Uncertain	-
952	Strong	B-H out of plane bend	Lehmann ³⁰ , Bell ³¹
679	Strong	B-C stretch	Siebert ³²

B-H_t refers to the terminal H on B (normal B-H bond) and B-H_b refers to a boron-bridging hydrogen.

The especially significant feature here is the splitting of the terminal B-H stretching frequency, for this indicates the presence of an RBH_2 form, wherein the two B-H bonds have the same structural status. The nearest literature analogue is found in the spectra of $(\text{CH}_3)_2\text{BH}\cdot\text{BH}_3$ and $\text{CH}_3\text{BH}\cdot\text{BH}_3$, which show the splitting characteristic of the BH_2 unit, whereas the type $(\text{RBH}_2)_2$ (1,2-dialkyldiboranes) do

not show such a doublet.²⁹ But a frequency characteristic of the $\begin{array}{c} \text{H} \\ | \\ \text{B} \cdots \text{B} \\ | \\ \text{H} \end{array}$ bridge

also appears in the spectrum of our phosphinated ethylborine. Hence we can only conclude that there is an equilibrium between the RBH_2 form (presumably having an internal P-B dative bond) and the 1,2-dialkyldiborane type $(\text{RBH}_2)_2$. It is also of interest that the bridge-stretching frequency is distinctly weaker than the B-H_t frequencies, whereas in the literature examples where they appear in the same compound, they are equally strong. Hence it is suggested that the bridged dimer is not favored in this equilibrium; the monomer seems to predominate.

Another interesting feature is the band at 679 cm^{-1} , which seems to represent the B-C stretching. This serves as further evidence that the BH_3 group entered the ethylenic double bond as H and BH_2 , rather than forming a BH_3 complex with phosphorus.

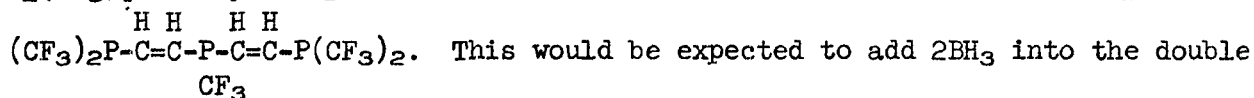
The band at 1383 cm^{-1} can be attributed to B-O stretching, for some fogging of the KBr pellet suggested hydrolysis. The assignment corresponds to 1360 , 1361 , and 1372 cm^{-1} respectively for $\text{HB}(\text{OCH}_3)_2$, $\text{B}(\text{OCH}_3)_3$, and $\text{ClB}(\text{OCH}_3)_2$ - or 1400 , 1425 , and 1429 for $\text{B}(\text{i-C}_3\text{H}_7\text{O})$, $\text{B}(\text{OC}_2\text{H}_5)_3$, and $\text{HB}(\text{OC}_2\text{H}_5)$.

The strong bands at 1013 and 1040 cm^{-1} remain ambiguous because they seem too low to represent a further splitting of the C-F stretching frequencies (Table XXIX) and also too low for the B-H bend-in-plane vibration, found in diborane at 1154 , 1178 , and 1197 cm^{-1} . They seem a little too high to be surely assigned to C-H bending of some kind.

The molecular weight of this diphosphinoethylborine could not be determined by the direct gas-density method because it proved not to be sufficiently volatile for work at temperatures low enough for dependable stability. However it did prove to be soluble enough in methyl bromide for a fairly good indication of the molecular weight in that solvent. The 0.277 mmole sample was dissolved in 48.21 mmoles of CH_3Br and at 21.1°C . the vapor tension of the solution was 6.4 mm. lower than that of the pure solvent (1334.4 mm.). The indicated mole fraction was 0.0048 for the solute, implying a molecular weight value of 445 . This corresponds to a monomer:dimer ratio of 82.18 , qualitatively in agreement with the indication from the infra-red spectrum. This is the first known case of a measureable equilibrium of the type $2\text{RBH}_2 \rightleftharpoons (\text{RBH}_2)_2$, and even here it is a case of dissociation of the $(\text{RBH}_2)_2$ form to make a complex with a base - which in this case happens to be supplied by the same molecule.

An Attempt to Make a Tetra-Phosphino-Ethane. Since C_2H_4 so easily absorbs $\text{P}_2(\text{CF}_3)_4$ to make the diphosphinoethane, it seemed possible that the acetylene product $(\text{CF}_3)_2\text{PC}_2\text{H}_2\text{P}(\text{CF}_3)_2$ could be made to absorb $\text{P}_2(\text{CF}_3)_4$ in a similar manner to form $[(\text{CF}_3)_2\text{P}]_2\text{C}_2\text{H}_2[\text{P}(\text{CF}_3)_2]_2$. However, this addition of $\text{P}_2(\text{CF}_3)_4$ to the ethylenic diphosphine seems to be far more difficult than the addition of diborane to the same diphosphine, for the reactants were recovered quantitatively after 4 days at 100°C ., even with a trace of iodine added for catalysis. During six days at 150°C ., the same mixture showed about 5% of reaction, forming primarily more

Taking all of the evidence together, it seems beyond doubt that the $P_2(CF_3)_4$ -acetylene product with mol. wt. near 490 has the structural pattern



bonds, as observed; and the boron atoms would have RBH_2 status, as shown by the acid-methanol reaction. The monomeric form of the boron compound might be formulated in any of three ways: with the BH_2 units on the carbon atoms farthest from the central phosphorus, with both BH_2 units on the inner carbon atoms, or with one BH_2 on a near carbon and the other on a far carbon. Then such units should be bound together fairly strongly by attaching a boron of one unit to the rather strongly basic central phosphorus atom of the next unit, thus making a polymer chain of infinite length. But this chain would still have an RBH_2 type of boron

hydride group on each unit. Hence there would be much $\begin{matrix} H \\ B \\ H \end{matrix}$ bridging between chains, for cross-linking. However, both the chain formation and the bridging cross-links would have to compete with a tendency to form a monomer by P-B dative bonding within the monomer unit. One can also see many possibilities for completing rings and developing bridge-versus-dative-bonding equilibria like that indicated in a simple way in the case of $(CF_3)_2PCH_2CHBH_2P(CF_3)_2$. Thus the true state of this double BH_3 adduct of the triple phosphine must be fantastically complex, and it is not in the least surprising that the material has the physical character of a resin.

The Fraction Having M.W. 454. The very small fraction having M.W. 454 (Table XXVII) seemed to be uniform, for its vapor tensions (Table XXXIII) had a normal trend: $\log_{10}P_{mm} = 7.9195 - 2434/T$; b.p. $220^\circ C$. and Trouton constant 23.1 ca./deg.mole.

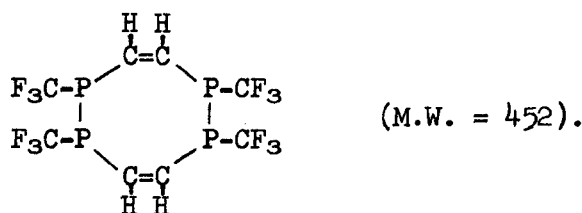
TABLE XXXIII

Vapor Tensions of M.W. 454 Fraction

t ($^\circ C$.)	35.0	48.6	56.8	64.5	75.3
P_{mm} (obsd.)	1.1	2.2	3.5	5.2	8.6
P_{mm} (calcd.)	1.1	2.3	3.5	5.2	8.6

The material formed a glass on cooling. Its ultra-violet spectrum has a peak at 2280 \AA ., with $\epsilon = 7830$, again suggesting two ethylenic links. The minimum is at 2135 \AA . ($\epsilon = 6280$). The presence of two C=C units per molecule was confirmed by its absorption of 0.058 mmole of B_2H_6 per 0.056 mmole sample, again producing a resin-like product.

A structural formula which would agree with these facts would be



This might seem improbable since its formation requires loss of CF_3 groups from both P atoms in $\text{P}_2(\text{CF}_3)_4$, and a highly fortuitous combination of two $\text{P}_2(\text{CF}_3)_2$ units with two molecules of acetylene; hence if it is correct, the very low yield is not surprising.

The Fraction Having M.W. 408. The slightly larger fraction having M.W. 408 (Table XXVII) also seemed to be a uniform substance, for its vapor tensions trended normally: $\log_{10} P_{\text{mm}} = 7.5800 - \frac{2173}{T}$ (b.p. 189°C .; Trouton constant, 21.5 cal./deg. mole). However, the range was very short (2.3 mm. at 27.4° , 3.9 mm. at 38.0° , 6.7 mm. at 48.6° , and 10.1 mm. at 57.2°C .; calcd. values, 2.3, 4.0, 6.7, and 10.1), and good conformity to this type of equation is unusual for such a low-pressure region.

The ultra-violet spectrum showed increasing absorption from 2700 to 2300 Å., and then a plateau from 2300 to 2100 Å., followed by the usual rise toward shorter wave lengths. Too little is known of the material for any speculation as to its structure. Although its M.W. and room-temperature volatility are similar to $(\text{CF}_3\text{P})_4$, its liquid character and different spectrum clearly distinguish it from this known substance.

The Tan Non-Volatile Oil. Both of the $\text{C}_2\text{H}_2\text{-P}_2(\text{CF}_3)_4$ experiments yielded a tan-colored non-volatile oil. From the approximate reaction-balance of the first experiment, the rough empirical formula of this oil would be $(\text{CF}_3)_4(\text{C}_2\text{H}_2\text{P})_3$, and from the second (reaction balance of Table XXVII, neglecting the small unidentified fractions) it would be $(\text{CF}_3)_{18}\text{P}_{11}(\text{C}_2\text{H}_2)_8$. Between these there is ample room to consider polymer chains having the general formulation $(\text{CF}_3)_2\text{P}(\overset{\text{H}}{\underset{\text{CF}_3}{\text{C}}}=\overset{\text{H}}{\underset{\text{CF}_3}{\text{C}}})_n\text{P}(\text{CF}_3)_2$.

A sample of the $(\text{CF}_3)_{18}\text{P}_{11}(\text{C}_2\text{H}_2)_8$ material, the weight of which was calculated as 276 mg., was heated for one week at 150°C ., to yield 170.6 mg. of $[(\text{CF}_3)_2\text{PC}_2\text{H}_2]_2\text{PCF}_3$ (0.24 mm. at 26°C .) along with 2.2 mg. of more volatile material not identified. This formation of the bis(phosphinovinyl)phosphine is favorable to the idea that the tan product also has a $\text{P-C}_2\text{H}_2\text{-P-C}_2\text{H}_2\text{-P}$ type of polymer skeleton.

The Iodine Method of Analysis. There was a need for a better method of determining CF_3 groups, for the basic hydrolysis often proved to be too slow and sometimes incomplete when the phosphorus atom carried a hydrocarbon group. The known ability of I_2 to remove CF_3 groups from $(\text{CF}_3)_3\text{P}$ on heating made it seem likely that a similar reaction could be brought to completion with our hydrocarbon-connected CF_3 -polyphosphines. In view of the C-H bonds in these compounds, it seemed possible that the CF_3 groups would come out not as CF_3I , but also to some extent as HCF_3 ; however one still could get a good estimate of the CF_3 groups provided that all of them were so removed from the phosphorus and not destroyed by disruption of C-F bonds.

The procedure was simply to heat the weighed sample with an excessive proportion of iodine in a sealed tube for a long enough time at 260°C ., and then isolate the HCF_3 and CF_3I for measurement. Table XXXIV shows the results of five such runs.

It appears that the iodine method goes more easily for the C_2H_2 -connected polyphosphines than for $(CF_3)_2PC_2H_4P(CF_3)_2$, but this also approaches quantitative completion if the heating is sufficiently thorough. The distinct superiority of the iodine method over basic hydrolysis, at least for the C_2H_2 -connected polyphosphines, is shown by comparison with the results shown in Table XXXV.

TABLE XXXIV

Iodine Method of CF_3 -Group Analysis

Compound	Sample (mmoles)	I_2 (mg-atoms)	Time at $260^\circ C.$	Products (mmoles)		Percent Recovery of CF_3
				HCF_3	CF_3I	
$(CF_3)_2PC_2H_4P(CF_3)_2$	0.094	5.555	16 hrs.	0.177	0.156	88.6
same	0.136	7.438	3 days	0.263	0.251	94.5
same	0.350	7.543	7 days (a)	1.250	0.132	98.7
$(CF_3)_2PC_2H_2P(CF_3)_2$	0.150	5.264	3 days	0.298	0.300	99.7
$[(CF_3)_2PC_2H_2]_2PCF_3$	0.071	8.014	3 days	0.214	0.132	97.7

(a) at $305^\circ C.$

TABLE XXXV

Basic Hydrolysis of Phosphines

Compound	Sample (mmoles)	Time at $100^\circ C.$	HCF_3 (mmoles)	Percent CF_3 recovery
$(CF_3)_2PC_2H_4P(CF_3)_2$	0.119	40 hrs.	0.453	95.2
$(CF_3)_2PC_2H_2P(CF_3)_2$	0.262	24 hrs.	0.927	88.5
$[(CF_3)_2PC_2H_2]_2PCF_3$	0.064	96 hrs.	0.283	88.4
$(CF_3)_2PC_2H_2CF_3$	0.106	17 hrs.	0.207	97.6(a)

(a) Assuming that a $C-CF_3$ bond would not be broken.

Discussion of Significance. The ample evidence that the reaction of acetylene with $P_2(CF_3)_4$ yields polyphosphines having one, two, or even more borane-active $C=C$ units leads to the hope that resins could be made from pentaborane-9 reacting with such poly-olefinic-polyphosphines. The isolated $C-C$ connections between boron-hydride polymer clumps should be as resistant to elevated temperatures as our known $P-B-H$ resins, and should lend mechanical strength. The presence of CF_3

groups in such polymers might be a source of instability, but we have frequently noticed that what can be done fairly easily with $\text{CF}_3\text{-P}$ compounds often can be managed also with methyl compounds of the same type, if some extra effort is made. The fluorocarbon approach often serves to demonstrate what might reasonably be tried with the less electronegative hydrocarbon groups on phosphorus.

The Reaction of $(\text{CF}_3\text{PH})_2$ with Ethylene

It was considered possible that the biphosphine $(\text{CF}_3\text{PH})_2$ would add to the double bond of ethylene in the same manner as $\text{P}_2(\text{CF}_3)_4$ does, thus giving a potentially valuable diphosphine having the formula $\text{CF}_3\text{PC}_2\text{H}_4\text{PCF}_3$. It happened that a small sample of $(\text{CF}_3\text{PH})_2$ was available from an attempt to repeat the preparation of $\text{C}_2\text{H}_4\text{O}_2\text{PCF}_3$ (Ref. 4, p. 103), so that it was convenient to explore its reaction with ethylene. The glycol reaction of $(\text{CF}_3\text{P})_4$ in tetralin at 100°C . this time gave a 70% yield of the triphosphine $\text{H}_2(\text{CF}_3\text{P})_3$ (based on the used-up tetramer—an improvement over the earlier 50%, ascribed to more frequent removal of the product), and this triphosphine was easily converted to the biphosphine by the previously—mentioned tertiary-phosphine catalysis. The failure to get any of the desired $\text{C}_2\text{H}_4\text{O}_2\text{PCF}_3$ is ascribed to a trace of water in the tetralin, which was handled in the open for convenience.

In the actual experiment on $(\text{CF}_3\text{PH})_2$ with C_2H_4 , it seemed that some of the desired diphosphine was formed, but this was far from all that happened. The mixture of 0.509 mmole of $(\text{CF}_3\text{PH})_2$ and 1.603 mmoles of C_2H_4 was warmed rapidly from -196°C ., forming a fog indicative of fast reaction. Successive fractions:

1. C_2H_4 - - - - - 1.023 mmoles (used 0.580 mmole)
2. CF_3PH_2 - - - - - 0.068 mmole (identified by M.W. and volatility)
3. $\text{C}_2\text{H}_5\text{CF}_3\text{PH}$ - - - 0.167 mmole (presumed formula; M.W. 139 vs. 130)
4. $\text{C}_2\text{H}_5(\text{CF}_3\text{P})_2\text{H}$ - - 0.040 mmole (supposed; M.W. 216 vs. calcd. 230)
5. $\text{CF}_3\text{PC}_2\text{H}_4\text{PCF}_3$ - - 0.112 mmole (supposed; M.W. 227 vs. calcd. 230)

$\text{H} \quad \text{H}$
6. Oil which refluxed on heating in vacuo.

Fraction 3 was converted to the BH_3 complex, which next was heated at 100°C ., evolving H_2 in amount corresponding to the formation of $\text{C}_2\text{H}_5\text{CF}_3\text{PBH}_2$ units. The product melted in a plastic manner and was not appreciably volatile at 100°C . Fraction 4 showed a vapor tension of 4 mm. at 0°C ., whereas fraction 5 had only 0.34 mm. vapor tension at 0°C . Its other vapor tensions gave the equation $\log_{10}P_{\text{mm}} = 7.848 - 2272/T$ (b.p. 184°C .; Trouton constant 22.7 cal/deg.mole). A neater experiment will be possible when a new supply of $(\text{CF}_3\text{PH})_2$ becomes available. In the meantime the three new compounds here indicated must be regarded as entirely speculative in regard to constitution.

SUMMARY

For the synthesis of $P_2(CF_3)_4$ from $(CH_3)_2NP(CH_3)_2$ and $(CH_3)_2PH \Delta F^\circ = 1.79 + 0.00226T$ kcal./mole, implying yields of 84 and 89% at 99 and 26°C. Further work on the conversion of $P_2(CH_3)_4$ to $(CH_3)_2PC_2H_4P(CH_3)_2$ (m.p. 0°C.; b.p. 188°C.) is described. This diphosphine was used with $(CH_3)_3P$ and B_5H_9 for preferential incorporation in a boron-hydride resin containing no $(CH_3)_3P$. The mechanical superiority of this resin is ascribed to some double-base action by the diphosphine. Attempts to make a $(CF_3)_2PSCF_3$ for work with B_5H_9 did not succeed.

The chloro-cyclo-phosphine C_4H_8PCl (low-temp. glass; b.p. est. 165°C.) was made from $(CH_3)_2NPC_4H_8$. Its characterization completes the data for a publication on C_4H_8P - compounds.

The reaction of $(CF_3)_2PI$ with Ag_2CO_3 gives the new-type diphosphoxane $(CF_3)_2POP(CF_3)_2$ (m.p. -53°C.; b.p. 78°C.) and this reacts with HCl to give another new type, the acid $(CF_3)_2POH$ (m.p. -21°C.; b.p. 61°C.), in yields above 90%. The I.R. spectra of these confirm the indicated structures and neither compound shows any tendency to rearrange to a phosphine oxide form or to disproportionate— reactions which prevent isolation of the corresponding $(CH_3)_2P$ - compounds. An obvious reason for the difference is the lack of base strength of P in the $(CF_3)_2P$ - compounds; the diphosphoxane actually behaves as a Lewis acid toward $(CH_3)_3N$, which reacts also with $(CF_3)_2POH$ to make a stable $(CH_3)_3NH^+$ salt. The diphosphoxane adds to C_2H_4 to make some $(CF_3)_2POC_2H_4P(CF_3)_2$ (m.p. 5°C.; b.p. 202°C.) and unknown by-products. The reaction of $(CF_3)_2POH$ with $(CH_3)_2PH$ gives $(CF_3)_2PH$ and the disproportionation products of $(CH_3)_2POH$, confirming predictions from last-year's acid-cleavage of $(CH_3)_2PP(CF_3)_2$. Similarly as predicted is the reaction of $(CH_3)_2PH$ with $P_2(CF_3)_4$ to give $(CF_3)_2PH$ and $(CH_3)_2PP(CF_3)_2$, and eventually $P_2(CH_3)_4$. However, the reaction of $(CH_3)_2PH$ with $(CF_3)_2POP(CF_3)_2$ does not lead to isolation of any methylated diphosphoxanes. Instead, the first step seems to form $(CF_3)_2POH$ and $(CH_3)_2PP(CF_3)_2$, but these react to produce $P_2(CF_3)_4$ and what seems to be $(CH_3)_2P-P(CH_3)_2$ (m.p. 133°C.; inert to O_2 ; vacuum sublimable at 100°C.); then in

0 0

the main reaction the $P_2(CF_3)_4$ is converted by $(CH_3)_2PH$ to $(CF_3)_2PH$ and $(CH_3)_2PP(CF_3)_2$ as before.

The removal of CF_3 groups from phosphorus (III) by the action of Br_2 is understood in terms of formation of the phosphoranes $(CF_3)_nPBr_{5-n}$, which lose CF_3Br in reverting to phosphorus (III) compounds. Several intermediate and parallel processes can be recognized. The transfer of Br_2 from $(CF_3)_3PBr_2$ to $(CF_3)_2PBr$, from $(CF_3)_2PBr_3$ to CF_3PBr_2 , and from CF_3PBr_4 to PBr_3 correlates with greater stability for phosphoranes having more Br and fewer CF_3 groups. Mercury attacks $(CF_3)_2PBr_3$ to make $(CF_3)_2PBr$ which reacts with mercury only if heated; but CF_3PBr_2 reacts with mercury at room temperature to make $(CF_3P)_n$ rings. These are formed also from CF_3PI_2 or CF_3PBr_2 with antimony or from CF_3PCl_2 with $(CH_3)_3Sb$. A similar dechlorination by $(CH_3)_3Sb$ converts $(CF_3)_2PCl$ to $P_2(CF_3)_4$. Conversion of $(CF_3)_2PCl$ to $(CF_3)_2PI$ can be done through formation of $(CF_3)_2PNH_2$ for reaction with HI ; and CF_3PH_2 can be made by the action of PH_3 on CF_3PI_2 .

The monomer-complex $(CH_3)_3PPCF_3$ with HCl gives CF_3PH_2 , CF_3PCl_2 , possibly CF_3PHCl , and non-volatiles. The far slower CH_3Cl reaction seems to give $(CH_3PCF_3)_2$ and higher phosphines. The rapid CH_3I addition gives what seems to be $(CH_3)_3PPCH_3CF_3^+I^-$, for this solid reacts with HCl to give CH_3CF_3PCl (b.p. 51°C.),

which is convertible to $(\text{CH}_3)_2\text{NPCH}_3\text{CF}_3$ (b.p. $99^\circ\text{C}.$)— and back by action of HCl . The decomposition of $(\text{CH}_3)_2\text{NPCH}_3\text{CF}_3 \cdot \text{BH}_3$ is being explored. Formation of $(\text{CH}_3\text{PCF}_3)_2$ from CF_3PI_2 , CH_3I , and Hg may have succeeded but the supposed $(\text{CH}_3\text{PCF}_3)_2$ differs from the product of the $(\text{CH}_3)_3\text{PPCF}_3\text{-CH}_3\text{Cl}$ reaction. The reaction of CF_3PCl_2 with $(\text{CH}_3)_2\text{NH}$ gives $(\text{CH}_3)_2\text{NPCF}_3\text{Cl}$ (b.p. $115^\circ\text{C}.$).

In the nearly quantitative formation of $(\text{CF}_3)_2\text{PC}_2\text{H}_4\text{P}(\text{CF}_3)_2$ (m.p. $-51^\circ\text{C}.$; b.p. $135^\circ\text{C}.$), both light and heat favor the migration of CF_3 groups to form $(\text{CF}_3)_3\text{P}$, $[(\text{CF}_3)_2\text{PC}_2\text{H}_4]_2\text{PCF}_3$ (0.2 mm. at $24^\circ\text{C}.$), and non-volatile oils probably having a $(=\text{PC}_2\text{H}_4-)_n$ skeleton. The weakly basic diphosphine $(\text{CF}_3)_2\text{PC}_2\text{H}_4\text{P}(\text{CF}_3)_2$ seems to form a resin during a slow reaction with diborane.

The I_2 -catalyzed $\text{P}_2(\text{CF}_3)_4\text{-C}_2\text{F}_4$ reaction also forms a diphosphine, $(\text{CF}_3)_2\text{PC}_2\text{F}_4\text{P}(\text{CF}_3)_2$ (m.p. $-49.6^\circ\text{C}.$; b.p. $127.0^\circ\text{C}.$), but side reactions involving C-chain-building and migration of fluorocarbon groups are far more pronounced, forming $(\text{CF}_3)_3\text{P}$, C_4F_8 , cyclo- $\text{C}_4\text{F}_8\text{PCF}_3$, and unidentified less volatile material. Such CF_3 -migration is found also in the conversion of $(\text{CF}_3)_3\text{P}$ by phosphorus (I_2 -catalyzed) to a good yield of $\text{P}_2(\text{CF}_3)_4$.

The I_2 -catalyzed $\text{P}_2(\text{CF}_3)_4\text{-C}_2\text{H}_2$ reaction gives an even wider variety of products, some having much promise for use in making BH resins. The main product (60%) is the 1,2-diphosphinoethylene $(\text{CF}_3)_2\text{PC}_2\text{H}_2\text{P}(\text{CF}_3)_2$ (m.p. $-54^\circ\text{C}.$; b.p. est. $122^\circ\text{C}.$), the I. R. Spectrum of which indicates only the trans- isomer. It easily takes H-BH_2 into the double bond, and the resulting RBH_2 compound exists chiefly

as a monomer (presumably with a P-C-C-B ring) in equilibrium with less of a $\begin{matrix} \text{H} & & \text{H} \\ & \diagdown & / \\ \text{B} & & \text{B} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{matrix}$ bridged dimer. By way of contrast, $\text{P}_2(\text{CF}_3)_4$ fails to add to the P-C=C-P double bond. The by-products of the $\text{P}_2(\text{CF}_3)_4\text{-C}_2\text{H}_2$ reaction include $(\text{CF}_3)_3\text{P}$ and the new $(\text{CF}_3)_2\text{PC}_2\text{H}_2\text{CF}_3$ (low-temp. glass; b.p. $74^\circ\text{C}.$, for which I.R. shows cis-trans isomers. This latter can be made also by an I_2 -catalyzed addition of $(\text{CF}_3)_3\text{P}$ to C_2H_2 . Still another $\text{P}_2(\text{CF}_3)_4\text{-C}_2\text{H}_2$ by-product is $\text{CF}_3\text{P}[\text{C}_2\text{H}_2\text{P}(\text{CF}_3)_2]_2$ (low-temp. glass; b.p. $203^\circ\text{C}.$), both double bonds of which take on H-BH_2 . This bis(phosphinovinyl)phosphine suggests a polymer principle which would explain other by-products, including the tan non-volatile oil.

The addition of $(\text{CF}_3\text{PH})_2$ to C_2H_4 has been explored but the interpretation of the results is speculative.

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